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**Review**

# The current state of silicone-based dielectric elastomer transducers

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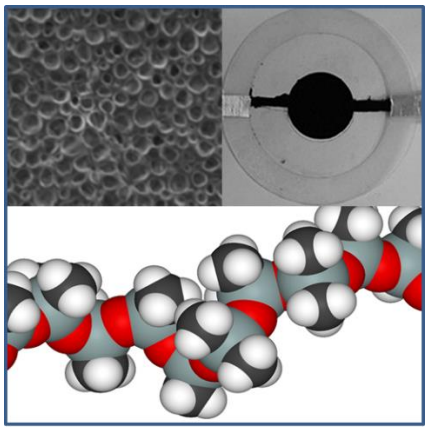
Silicone elastomers are promising materials for dielectric elastomer transducers (DETs) due to superior properties such as high efficiency, reliability and fast response times. DETs consist of thin elastomer films sandwiched between compliant electrodes, and they constitute an interesting class of transducer due to their inherent lightweight and potentially large strains. For the field to progress towards industrial implementation, a leap in material development is required, specifically targeting longer lifetime and higher energy densities to provide more efficient transduction at lower driving voltages. In this review the current state of silicone elastomers for DETs is summarised and critically discussed, including commercial elastomers, composites, polymer blends, grafted elastomers and complex network structures. For future developments in the field it is essential that all aspects of the elastomer are taken into account, namely dielectric losses, lifetime and the very often ignored polymer network integrity and stability.



## 1. Introduction

The search for materials that exhibit properties similar – or even superior – to the human muscle has been the focus of engineers and researchers for several decades. The challenge lies in the many excellent properties of human muscles, such as high energy densities and large, obtainable strains. Furthermore, human muscles generate linear motion, whereas currently used electric motors generate rotational motion.[1–3] Another feature of human muscles is that they have self-repairing properties, which is also highly desired for soft transducers.

Polymers offer interesting prospects as smart materials for artificial muscles, as they are lightweight, noiseless and low in cost. Electroactive polymers (EAPs) consist of soft polymeric materials with relatively large energy densities, relatively fast response times and the ability to undergo large deformations when stimulated by electrical fields.[4,5] EAPs can be divided into two main groups: ionic and electronic. Ionic EAPs respond to an electrical field through the diffusion of ions in a material. In addition, they generally require low driving voltages (as low as 1-2 V) but require an electrolyte, which means that encapsulating the aqueous environment is necessary. Furthermore, there is a need to maintain wetness, and it is difficult to maintain DC-induced displacements.[6–9] However, recent developments[10] have proven it possible to create semi-interpenetrating networks from polyionic liquids, which eliminates the need for an aqueous environment and thereby opens up the possibility of a wide range of applications where large forces are not needed. The advantages of electronic EAPs over their ionic counterparts include higher energy density, that they can be operated in air without major constraints, large actuation forces, rapid response times and long lifetimes. Their major disadvantage is that they require high driving voltages to actuate (typically 500 V to 10 kV),[4,11] and so a great deal of research focuses on reducing this issue. Electronic EAPs can be divided further into subclasses, such as polymer electrets,[12–14] electrostrictive graft elastomers[15] and dielectric elastomers. In the field of electronic EAPs, dielectric elastomers are a very interesting class of material, due

to high obtainable actuation speeds, large strains and high work densities, a high degree of electromechanical coupling and good overall performance.[16,17] As a result of this unique combination of properties, dielectric elastomers occupy a niche in transducer technologies, mainly due to their low weight coupled with large strains. The focus of this review is therefore exclusively on dielectric elastomers.

Dielectric elastomers are promising materials for advanced electromechanical applications such as actuators, generators and sensors, due to their simple and flexible working principle. They consist of an elastomer film sandwiched between two thin and compliant electrodes, thereby forming a capacitor capable of energy transduction. The electrodes can be made from a variety of conducting materials such as silver and gold[18,19] and carbon grease.[17] For more details on electrode systems an excellent recent review on electrode materials by Rosset and Shea[20] exists. In this review we refer to the system of elastomer and electrode as a 'dielectric elastomer transducer' (DET). When an external voltage is applied to the electrodes, electrostatic forces are created. Electrostatic pressure acting on the film squeezes the elastomer in thickness, and as the elastomer is incompressible it consequently expands in planar directions. Electrical energy, in this case, is thus converted into mechanical energy. The driving force for the actuation process is the resulting reduction in charge density when the electrode area is enlarged.[21] When the external voltage is switched off, the elastomer film returns to its original shape. The actuation working principle can be seen in **Figure 1**.

Dielectric elastomers can also be used for generators to create electrical energy, if the DET is stretched by an external force and electrical charges are placed on the film.[22,23] When the DET is allowed to relax, elastic stresses work against electrical field pressure, thereby increasing electrical energy. In this process opposite charges on the two electrodes are pushed further apart as the film contracts and increases in thickness, while similar charges are brought closer together as a result of the decreasing area of the elastomer, thus increasing energy density. These changes increase the voltage of the charge, and the created energy can be harvested.[24]

DETs have the potential to be used in novel applications which have not been possible previously or feasible through the use of other technologies. Especially within the actuator application area, DETs could provide novel solutions such as flat screen loud speakers,[25] lightweight morphing structures and prosthetic-like actuation, especially due to the flexibility of the material, which offers the ability to be formed into complex shapes and still provide actuation.[26–29] Other DET applications range from valves and pumps[30] to (bio-mimicking) robotics,[31–33] Braille displays,[34–36] adaptable lenses and gratings,[37] motion sensors,[38] wave energy harvesting[24] and active vibration control.[39] The main advantage of DETs in these applications over other transducers, however, is their ability for large displacements. In **Figure 2** two examples are presented showing the extraordinary behaviour of dielectric elastomers, namely a flying fish by the Swiss Federal Laboratories for Materials Science and Technology, EMPA,[40] illustrating the lightweight nature, and a wave-harvesting unit capable of large strains.[41]

One of the most important components of a DET is the elastomer, as it governs dielectric permittivity, dielectric breakdown strength and (in combination with the electrodes) obtainable strain. Silicone elastomers are one of the most used materials for DETs due to their high efficiency, reliability and fast response times.[4,42] Other materials commonly used include acrylic elastomers (such as VHBs from 3M) and polyurethane elastomers. The major advantage of silicone elastomers over other materials is that they produce repeatable, reproducible actuation upon activation, they show little tendency for Mullins (stress softening) and ageing effects and they have been shown to actuate (at low strains) to more than 4 million cycles, in some instances more than 10 million cycles, without failure.[3,43,44] They also possess significantly lower viscous losses than acrylics, indicating that they can be operated at higher frequencies with lower losses and less heat generation. Furthermore, silicones can be operated at a broader temperature range[4] and possess inherent softness and stability. The disadvantage

of silicone elastomers is that they possess relatively low dielectric permittivity, which means that a higher electrical field is needed to actuate the DET to obtain a given strain.

Generally speaking, the dielectric permittivities of current dielectric elastomers range from 2 to 8, while silicone elastomers typically have dielectric permittivity at around 2-3. This means that silicone elastomers, despite possessing superior mechanical properties compared to other dielectric elastomers, do not reach their full potential due to their energy density being too low (i.e. too low dielectric permittivity). The practically obtained actuation strain of silicone DETs is thus usually less than 15% (if not pre-strained), while elongations up to 300% should be realisable, provided that the elastomer survives electrically.

The silicone elastomers currently used for DETs are off-the-shelf materials, and as such they have not been developed for use in this specific application and are not the result of targeted development. Therefore, recent years have seen a large increase in research on and the development of silicone materials for DETs, namely where commercial silicone elastomers have been modified and where new silicone elastomer formulations have been prepared.

While several excellent reviews and overviews about EAPs exist,[4,45–49] this review aims specifically at providing a comprehensive overview of recent developments with silicone elastomers for DETs. Silicone elastomers are often highlighted as the most suitable and promising elastomer material for DETs; however, the benchmark for silicone dielectric elastomers is still commercial silicone elastomers, such as RT625 from Wacker Chemie AG and Sylgard 184 from Dow Corning. We hope that this review will pave the way forward in order for the field to progress and handle great challenges, such as the often ignored lifetime and electromechanical stability. Furthermore, the intent is that this overview will reduce the number of repetitive studies performed within the field and promote research into silicone elastomers in general by showing their strengths as dielectric elastomers.

First, a discussion of important dielectric parameters is undertaken, followed by a brief introduction to the chemistry and technology of silicones and silicone elastomers and a section-

wise description of the research that has been conducted on the use of silicones as DETs, including: commercial silicone elastomers, silicone composites, silicone blends, chemically modified silicones and advanced network structures such as interpenetrating networks and bimodal networks. The review is summarised by an outlook describing the potential of silicone DETs and the suggested next steps for the research community within the area.

### 1.1 Dielectric elastomer parameters

The equation for the actuation strain of DETs valid for small strains (usually less than 10%), developed by Pelrine et al.[50], correlates electrostatic pressure, $p_{el}$, to thickness strain, *s*, and the Young's modulus, *Y*, according to:

$$s = \frac{p_{el}}{Y} = \frac{\varepsilon_r \varepsilon_0}{Y}\left(\frac{U}{d}\right)^2 \quad (1)$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is vacuum permittivity, *d* is the thickness of the material, *U* is the voltage and $\varepsilon_r$ is the relative dielectric permittivity of the elastomer film defined as $\varepsilon_r = \varepsilon' / \varepsilon_0$, where $\varepsilon'$ is the real part of the dielectric permittivity of the material.

From Equation 1 it is clear that three material properties, namely dielectric permittivity, the Young's modulus and the maximum applicable voltage (the dielectric breakdown strength, $E_B = (U/d)_{max}$), govern the performance of a DET. It is important, however, to keep in mind that several other essential parameters remain unexposed in the actuation equation.

In particular, Equation 1 is valid for small strains only, since the Young's modulus depends not only on the applied strain for larger strains (usually higher than 10-30%, depending on the elastomer), but also on the applied strain rate, i.e. Y(s, δs/δt). In the linear regime, which for silicone elastomers is up to approximately 15% in strain,[51] elastic and viscous properties are well described by the shear storage modulus, *G'*, and the shear loss modulus, *G''*, defined from the complex shear modulus $G^* = G'(\omega) + iG''(\omega)$. Due to the incompressibility of silicones (Poisson's ratio (ν) close to 0.5), the Young's modulus can be determined as $Y = 2(1 + \nu)G$,

where $G = G'(\omega \rightarrow 0)$. Viscous loss, i.e. energy lost as heat into the surroundings, can be determined from $G''$ and is usually referred to via the loss tangent, $\tan \delta = G''/G'$. Silicone elastomers usually possess significantly lower viscous losses than acrylic elastomers.

The strain dependency of dielectric elastomers' permittivity is also often debated, but no coherent conclusion has been drawn so far.[52] Much of the inconsistency in dielectric data may be caused by the complexity of obtaining reliable, reproducible data on thin, flexible films. Nevertheless, the strain-dependency of the Young's modulus is usually significantly larger than that of the observed dielectric permittivity, and therefore dielectric permittivity is usually regarded as a constant. Since one of the major advantages of dielectric elastomers over other transducer materials is the possibility of achieving high strains, the use of models taking large strains into account is required for a satisfactory description of high-strain behaviour such as the models proposed in the references.[2,53–55] However, modelling is not discussed further in this review.

In principle a DET is a stretchable capacitor for which energy storage capacity is described by its capacitance, which in turn is defined by the dielectric permittivity of the dielectric elastomer. As mentioned in the introduction, dielectric permittivity is an important – if not *the* most important – factor for silicone elastomers that suffer from low dielectric permittivity compared to, for example, acrylic elastomers and polyurethanes. When an electrical field is induced, all materials become polarised. If the material is conducting, the electrical field will induce charge transport. In an insulator, such as a silicone elastomer, the elastomer can be considered as consisting of small dipoles with separate internal charges within an overall electrically-neutral material. The dipolar species consists of molecules that carry dipole moments or negatively charged species, such as electrons, anions and other chemical groups with negative partial charges, and positive species, such as atomic nuclei, cations and groups with positive partial charges. When subjected to an electrical field, the dipoles will align with the field, in order for the negative part of the dipole to orient towards the higher potential, while the positive part of

the dipole will orient towards the lower potential. Electrostatic energy created in the material is then converted into mechanical energy through different mechanisms, the simplest of which is Maxwell stress, whereby stress is proportional to the dielectric constant.[21]

The driving voltage that can be applied to a dielectric elastomer is limited by dielectric breakdown strength, $E_B = (U/d)_{max}$, which ideally is a material-specific constant, also denoted the inherent breakdown strength. Electrical breakdown mechanisms are complex, as they are dominated by extrinsic factors not inherent in the material, such as imperfections, as well as statistical variations in morphology and microstructure.[56–59] Recent modelling has focused on determining intrinsic breakdown strengths,[59] and a fundamental understanding thereof will lead to improved materials. Based on this fundamental knowledge, combined with continued progress in processing methods, electrical breakdown strengths closer to the intrinsic breakdown will become realisable.

High dielectric breakdown strength is desired so that the DET does not experience premature failure. This means that it is important for the elastomer to be free from impurities or voids that cause locally reduced dielectric strength. Since – in practice – it is impossible to avoid defects, $E_B$ depends strongly on elastomer film thickness, since the number of defects scales with volume and thus thickness.[60] Furthermore, it is important that the material exhibits low dielectric losses, which continuously contribute to the generation of heat in the material. If heat generated by these dielectric losses exceeds heat dissipated in to the surrounding area, the temperature in the elastomer will rise, which in turn could lead to thermal breakdown.[61] The structural order of the polymer network also influences dielectric breakdown strength. This is obtained through pre-straining the elastomer,[62] whereby the polymer chains are aligned and the maximum applicable electrical field is greatly increased.[57] Pre-straining is crucial for the actuation performance of, for example, acrylic elastomers,[62,63] since it simultaneously facilitates at least two properties favourable for improved actuation, namely reducing thickness and significantly increasing breakdown strength,[57] while the Young's modulus may decrease

significantly for strain-softening elastomers such as VHB and many soft silicone elastomers. In **Figure 3**, pre-straining devices are illustrated. In general, silicone elastomers do not show the same strong tendency to strain-softening as acrylics, and they are naturally soft from the un-stretched state. Therefore, pre-straining is not a prerequisite for the actuation of silicone elastomers. However, several studies have shown pre-straining to be very favourable for silicone elastomers.[62,64] A recent study by Zakaria et al.,[65] for instance, showed that the breakdown strength of two types of silicone elastomers was greatly improved by pre-straining, even when accounting for the reduction in thickness. It is therefore obvious that pre-straining introduces a favourable orientation for silicone elastomers and allows for the diffusion of volatile cyclic silicones out of the elastomer.[65] Pre-straining is also a common way to avoid electromechanical instability (EMI),[66] a matter which will be discussed later.

A factor not accounted for in the actuation equation is dielectric loss, $\varepsilon''$, which is commonly stated as the loss tangent, $\tan\delta = \varepsilon''/\varepsilon'$, where $\varepsilon''$ is the imaginary part of dielectric permittivity attributed to, among other things, dipole relaxation phenomena, which in turn gives rise to energy loss. Dielectric losses also influence the conductivity ($\sigma$) of the elastomer, where conductivity for insulating dielectric materials is dependent on dielectric loss and frequency ($\omega$) as $\sigma = 2\pi\omega\varepsilon''\varepsilon_0$. Silicones are in general electrically insulating materials, though no material can be considered as ideally insulating. Upon changing the molecular structure of the elastomer or adding high dielectric constant fillers, unwanted conductive paths – and thereby possible means of charge transport – can occur in the elastomer. Undesired conductivity, which can lead to large dielectric losses, results in the formation of conducting pathways and $\sigma$ becoming independent of frequency below a critical frequency $\omega_c$.[67]

Tear strength, especially for inherently soft silicone elastomers, is a very important material parameter which is not considered in the equation for actuation strain. It becomes crucial in processing, as the thickness of the elastomer films is reduced to increase transducer performance. In the commercial film coating process of Danfoss PolyPower the major

processing issue was high surface energies related to the release of the thin films with micro-structural corrugations from the carrier web.[68–70] Unsuccessful release usually caused the detrimental tearing of films. Also, when considering product reliability, the tearing of elastomer films after electrical breakdown is a crucial problem. Silicone elastomers may be partly self-healing upon electrical breakdown, but if they are torn, the film cannot, with current materials, be restored in a simple way.

With the vast number of important parameters, a direct comparison of different elastomers is difficult. Therefore, Sommer-Larsen and Larsen[71] defined a universal expression which, through a single parameter, the *figure of merit, $F_{om}$*, can be used to evaluate the performance of a DET at a constant potential. The figure of merit depends on the dielectric constant, dielectric breakdown strength and, for actuators, the elastic modulus (Young's modulus) of the elastomer material. The equations for figures of merit, to assess elastomer performance as a dielectric elastomer actuator (DEA),[71] and a dielectric elastomer generator (DEG)[72] are defined as follows:

$$F_{\mathrm{om}}(\mathrm{DEA}) = \frac{3\varepsilon'\varepsilon_0 E_{\mathrm{B}}^2}{\mathrm{Y}} \quad (2)$$

$$F_{\mathrm{om}}(\mathrm{DEG}) = \frac{\varepsilon'\varepsilon_0 E_{\mathrm{B}}^2}{2\varphi} \quad (3)$$

where φ is the strain energy function of the elastomer.

Of course, a more realistic figure of merit would also include maximum extensibility, tear strength, excessive heat dissipation (from losses), etc. In other words, the figure of merit should account for whichever failure occurs first. However, for silicone elastomers the maximum elongation is currently not the limiting factor for dielectric elastomer performance regardless of whether applying pre-straining or not.

## 1.2 Failure modes of dielectric elastomers

The failure modes of dielectric elastomers are not included in the actuation equation. Models have been used extensively to study the failure modes and instabilities present in DETs, including thermodynamic electromechanical instability (pull-in, EMI),[66,73–78] wrinkling and/or buckling,[74,75] mechanical rupture[75,76] and dielectric breakdown,[75,76] for varying actuator configurations. Silicone elastomers very rarely fail due to mechanical rupture as the initial failure mode, but they may tear easily upon dielectric breakdown. This tearing usually arises from a pinhole formed in the elastomer after electrical breakdown, due to the resulting inhomogeneous stress fields. An improved understanding of these failure modes is required for the design of actuators capable of operating in a safe regime, thus prolonging actuator lifetime. Various safety factors (β), for example presented as a percentage of the intrinsic breakdown strength, $U_{max} = \beta E_B$, have been assumed, but obviously the safety margin is not a universal parameter and depends rather on the configurations of both the dielectric elastomer with electrodes as well as the type of actuator. The highly deformable, capacitive elastomer exhibits complex nonlinear behaviour, and in voltage-controlled actuation the electrical field increases as the thickness of the elastomer reduces. Instabilities may result in inhomogeneous deformation due to bi-stable conditions, also denoted as snap-through.[79] In **Figure 4**, the electromechanical responses of three types of elastomers with different chain extensibility are shown. The plots illustrate stresses, namely elastic and Maxwell stress, across the film as a function of strain, alternatively represented as an electrical field at constant voltage. The physical interpretation of this voltage-stretch response is as follows: as voltage ($U$) increases, the DET responds to the applied voltage through an increase in strain ($\lambda$). When $U$ becomes sufficiently high, the same voltage induces an even higher electrical field; positive feedback then develops between a thinning dielectric elastomer and an increasing electrical field, indicating the onset of EMI. In voltage-controlled actuation, at EMI, the deformation of the elastomer will 'jump' locally from a small $\lambda$ to a very high $\lambda$. The elastomer may not survive

this instability due to dielectric breakdown. As such, maximum actuation strain may be severely limited by EMI. Hence, to increase maximum actuation strain, it is desirable to avoid the snap-through phenomenon, or to move the phenomenon to low strains, such that the EMI can be utilised as a favourable instability.[79]

Another often overseen failure mode is space charge (SC) accumulation, which is an important characteristic of a direct current (DC) insulator and can be detrimental to the performance and reliability of an insulating elastomer.[80] Space charging can result from a range of phenomena, but most importantly they include 1) charge injection from electrodes and from electrical stress enhancement, 2) a combination of current density and spatially inhomogeneous resistance, 3) the ionisation of species within the dielectric to form a hetero-charge and 4) polarisation in structures such as water treeing. Due to the large water permeability of silicone elastomers it is very hard to avoid water within the silicone elastomer in humid environments, so all four phenomena are relevant for silicone dielectric elastomers.

Good materials for DETs are those less susceptible to SC accumulation, i.e. elastomers, amongst other things, should preferably be dry and have similar levels of electrical resistance. This is a major obstacle for hygroscopic materials such as polyurethane-based elastomers.[47] Furthermore, it is also desirable that any accumulated SC will deplete as quickly as possible when electrical stress is removed.[80]

## 1.3 Chemistry and technology of silicone polymers and elastomers

As mentioned previously, several classes of elastomers are applied for DETs, such as acrylics, polyurethanes and silicones. Of these three main types of elastomer, the silicones have the most promising potential for DETs, due in particular to increased long-term stability and reliability, which are the areas where the greatest development has to take place in order for the field to progress from the current state of the art.

In order to exploit advantages from the use of silicones, continued development, taking all the different aspects of the polymer system into account, is required. Silicone polymers (polysiloxanes) are an interesting and important class of polymer in which polydimethylsiloxane (PDMS) is the most widely used.[81] Polysiloxanes are based on the repeating unit RR'SiO, where R groups can be different organic groups such as vinyl, phenyl, hydride and alkanes, with the most common group being the methyl groups, such as those found in PDMS.[82]

Polysiloxanes have many interesting properties, such as high thermal stability, chemical and biological stability and inertness, ozone and UV resistance, hydrophobicity, transparency, high gas permeability, low glass transition temperature and low surface tension.[83] Polysiloxanes do not, however, possess good mechanical properties, and they are therefore often used as components in other systems or cross-linked and solidified into three-dimensional polymer networks, namely elastomers, which are usually formed by end-linking telechelic polymer chains in cross-linking reactions. When the siloxane polymer chains are linked together in networks, they are no longer able to diffuse by reptation, and the network has the ability to return to its original shape after stress is applied, i.e. they possess elasticity. Silicone elastomers are viscoelastic materials and therefore exhibit properties as both elastic solids and viscous fluids, where usually the elastic contribution dominates. In general, this viscous behaviour results in the materials becoming more sticky and adhesive-like, and it also causes heat dissipation within the material, which may have a strong impact on electrical properties and

thus lead to premature failure. Additionally, mechanical stability and reliability will be strongly affected.

Polysiloxanes, and in particular PDMS elastomers, have found widespread use as adhesives,[84] membranes,[85] sealants[86] and surface treatments[87,88] for soft lithography[89] and as dielectric elastomers. The PDMS elastomers utilised in these diverse applications are usually prepared by hydrosilylation, radical or condensation reactions which form a PDMS network. The most commonly applied preparation technique is the hydrosilylation reaction, also known as an 'addition reaction', where –Si-H groups react with $-CH=CH_2$ groups, as seen in **Scheme 1**. Hydrosilylation reactions are usually catalysed by a platinum catalyst and have the advantage over, say, a condensation reaction, in that they are very efficient and do not form by-products, which means that voids – in principle at least – can be avoided during elastomer synthesis. Condensation reactions are usually slower than hydrosilylation reactions, and curing rates depend strongly on the atmospheric humidity level. Furthermore, there seems to be a tendency for condensation cure elastomers to have lower dielectric breakdown strengths, most likely due to residual low molecular weight compounds and voids left in the elastomer from the condensation reaction.

Polysiloxanes are usually prepared through the nucleophilic substitution of chlorosilanes, which leads to low molecular weight linear and cyclic siloxanes. These are reacted further into high molecular weight polymers by an acid- or base-catalysed equilibrium reaction. Thus, silicone polymers commonly contain small amounts of low-molecular weight residuals which usually remain in the final elastomer if precautions against this issue are not taken.[90] The most commonly utilised method for this is so-called 'post-curing', where the elastomers – after curing at normal conditions – are heated in an oven at an elevated temperature for several hours (usually more than 4 hours, depending on geometry). Zakaria et al.[65] showed that these low molecular weight compounds greatly influenced the dielectric breakdown strength of dielectric

elastomers. Upon removing residual compounds by post-curing, dielectric breakdown strength increased ~20% despite the sol fraction in the original elastomer constituting less than ~2%.

The most commonly employed hydrosilylation cross-linking system uses *f*-functional hydride-functional cross-linker molecules and vinyl-terminated PDMS. The functionality, *f*, of the cross-linker should be ≥3, in order to form a polymer network. The mechanical properties of a silicone network are governed primarily by the molecular weight of the PDMS chains, whereas the functionality of the cross-linker is less significant for cross-linkers with *f*>4 and no steric hindrance.[91] When very short polymers are cross-linked, the silicone elastomer becomes glass-like and brittle.[51] The stoichiometric imbalance (ratio between hydride and vinyl groups) may be used as a mechanical tuning parameter; however, it is important to keep in mind that by lowering the amount of cross-linker, a reduction in the Young's modulus is indeed obtained, though a large fraction of the elastomer will become a sol fraction, which in turn introduces both significant viscous losses and the possibility for significant silicone migration in products.[92]

Despite many other excellent properties, PDMS elastomers suffer from low tear and tensile strength and are therefore considered intrinsically weak. This is due to the low melting point of PDMS (−40°C), which means that above approximately −30°C the elastomer cannot reinforce itself through strain-induced crystallisation.[93,94] As a result, almost all applications require reinforcement of the elastomer with particles. The most common and efficient reinforcing filler for silicone elastomers is silica ($SiO_2$), which is added to elastomer systems in concentrations of 10-60 wt%. Other commonly used fillers for silicone elastomers include titania ($TiO_2$), zirconia ($ZrO_2$) and calcium carbonate ($CaCO_3$). The effectiveness of the reinforcement depends on the available surface area and the interaction between the filler and the base polymer, such as van der Waals forces and hydrogen bonding. The fillers lead to a higher degree of orientation and immobilisation of the polymer chains in the strained elastomer, and therefore

they reinforce the elastomer. Commonly unfilled silicone elastomers can be stretched less than 100%, and often significantly less, but when reinforced the extensibility increases dramatically. Commercial silicone elastomer systems can be divided into two classes, room temperature vulcanising rubber (RTV) and high temperature vulcanising rubber (HTV), based on their curing temperature. Traditionally, an RTV silicone is a condensation cure silicone; however, RTV silicones can also be addition cure silicones. Examples of RTV addition cure systems include Elastosil RT625, by Wacker Chemie AG, Sylgard 186, from Dow Corning, and Nusil's CF15-2186. As the name indicates, the characteristic of an RTV silicone cure system is that it will cure at room temperature, although the application of heat often decreases reaction time significantly. In order to obtain elastic, reliable elastomers, fast curing is required. This fast reaction 'freezes' in more elasticity (inhomogeneous stress fields are created and maintained) than slow curing, and thus the resulting mechanical properties are different despite reactions proceeding to the same extent. This is due to the presence of various interactions, mainly due to polymer chain entanglements, but particle-polymer and particle-particle interactions may also change, depending on curing conditions.

HTV can be cured by peroxides, addition cure or by a combination of mechanisms. Addition cure HTV silicone rubbers are further divided into the subclasses high consistency silicone rubber (HCR) and liquid silicone rubber (LSR), based on the degree of polymerisation. LSRs are lower viscosity systems and are ideal for complex moulds due to their flowability. Frequently used LSRs for DETs include Elastosil LR 3043/30 and 3043/50 from Wacker and Nusil's CF19-2186. More details on LSRs can be found in the work of Delebecq et al.[95,96]

It is commonplace for most addition cure systems that they usually come as two-part systems, namely an A part and a B part, where typically one part contains polymer and a cross-linker whereas the other part contains polymer and a catalyst. Upon mixing the two parts in ratios stated by the manufacturer, curing will take place. Furthermore, most commercial silicone

elastomers are highly filled (with silica and/or other reinforcing fillers or resins) and contain other additives such as inhibitors.

## 2. Commercial silicones for dielectric elastomers

The initial comparative study of dielectric elastomers, triggering research interest in improving the dielectric permittivity of silicone elastomers, was performed by Pelrine et al.[62] They compared two types of silicone elastomers with the acrylic elastomer VHB 4910 from 3M and showed how pre-straining was favourable for both silicones and acrylics, where dielectric breakdown strengths were shown to improve by 117% and 215%, respectively, from biaxial pre-straining. A larger study was performed subsequently by the same authors,[2] in which they conducted a comprehensive study on various types of elastomers, amongst others polyurethane, fluorosilicones, isoprene rubber and various types of silicone elastomers. The addition cure silicone elastomer Nusil CF192-2186, as a representative of RTV silicone elastomers, was shown to be an ideal candidate for dielectric elastomers, as it possessed the highest measured energy density and strain as well as better coupling efficiency, low creep and excellent tolerance to temperature and humidity.[97] A later study on Nusil CF192-2186 confirmed these results.[98] Michel et al.[99] later undertook a comparative study on Dow Corning's silicone elastomer DC 3481 and two 3M VHB acrylic elastomers. They concluded that the silicone elastomer possessed superior reproducibility, fast response rates and no frequency-dependent dissipation of work compared to acrylics. However, they also concluded that strains of more than 10% could not be obtained with this type of silicone elastomer, although acrylics could easily be actuated above 10% through a trade-off in relation to slow response, frequency-dependent dissipation and low reproducibility. A similar study was conducted by Molberg et al.,[52] who compared the commercial silicone elastomer Neukasil RTV-23 with a thermoplastic elastomer from styrene-isoprene block copolymers. Here, the focus was not on the highest achievable strain but rather on the small strain response at low frequencies and establishing how to obtain

frequency-dependent actuation. Again, silicone elastomers outperformed thermoplastic polymers with respect to overall performance. Zhang et al.[100] investigated the silicone elastomer DC 3481 with various amounts of three types of hardeners. They concluded that for their silicone elastomers optimal actuation was obtained for a pre-strain of 40% despite the elastomers showing strain-hardening behaviour, and the pre-strain therefore led to stiffer films, albeit an increase in dielectric breakdown strength strongly compensated for this result. An actuation response of almost 20% could be obtained at 40 V/μm for 40% pre-strained films.

Carpi and De Rossi[101,102] investigated a condensation cure elastomer, namely BJB TC5005. Very soft elastomers with a Young's modulus of 50 kPa and a dielectric permittivity of $\varepsilon' = 5$ were obtained. The same elastomer was investigated by Galantini et al.[103] together with a plasticiser in various combinations, which resulted in even softer elastomers.

Jordi et al.[104] compared three types of dielectric elastomer, namely the corrugated silicone elastomer film from Danfoss PolyPower (Wacker Chemie RT625 with 15 parts per hundred rubber (phr) silicone oil) and two other types of elastomer (VHB and a home-made acrylic interpenetrating polymer network (IPN) - for more details on IPNs see section: Systems with complex network structures – interpenetrating and bimodal networks). The authors concluded that VHB was by far the best material for actuation, but when achievable design cycles, creep behaviour and overall structural efficiency were taken into account, the picture changed and favoured the other two candidates. Taking practical restraints into consideration, the silicone became the favoured elastomer, as there was no need for heavy support structures to maintain the large pre-strains required for the IPN. In a similar study Berardi et al.[105] investigated the Danfoss PolyPower films[106–109] and came to the same favourable conclusions for silicones.

Skov et al.[110,111] investigated four different LSR elastomers and an RTV silicone elastomer, including the very tough LR 3043/50 which was concluded to be a suitable elastomer for energy generation due to its combined high mechanical and electrical strength as well as suitable flexibility. However, the elastomer reaction mixture was very viscous, which made solvent an

absolute requirement for thin film coating. Another LSR-type elastomer, namely Wacker Silpuran 6000/10 (medical grade), was investigated by Stoyanov et al.,[112] who reported similar advantages.

A recent study by Akbari et al.[113] on the effect of pre-straining silicone elastomers, with Sylgard 186 as the investigated elastomer, concluded that for silicone elastomers, large pre-strains were not as favourable as for VHB; rather, intermediate pre-strains should be used to avoid simultaneously the strong effect of strain-hardening as well as electromechanical instability (EMI). The elastomer should simply be coated thinner from the outset, in order to obtain the targeted, pre-strained film thickness. An overview of the discussed studies on commercial silicone elastomers is listed in **Table 1**.

## 3. Special home-made silicone formulations for dielectric elastomers

Only a few studies have focused on tailor-making silicone elastomers for dielectric elastomers. This may be due to the complexity of formulating elastomers, but it may also indicate that current commercial elastomers perform rather well. However, the commonly applied curing reaction, namely hydrosilylation, can be inhibited by the presence of nitrogen- and sulphur-containing substituents, and thus for the further functionalisation of silicone elastomers it may be convenient to change the curing chemistry to, for example, condensation curing[114] or UV curing.[115–119]

A common way of designing elastomers with improved mechanical properties for dielectric elastomers is to change the mixing ratio of the two components in the elastomer mixture. Elastomer mixtures are usually designed such that for the stated mixing ratio there is a slight excess of cross-linker, to allow for ideal cross-linking despite steric hindrance.[91] As described previously, the elastomer usually consists of a premix with PDMS, a catalyst and silica (denoted premix A here) and another premix with PDMS and a cross-linker (denoted premix B). By increasing the mixing ratio of A to B, cross-linker content is reduced. This method can be used

to decrease the Young's modulus, as it scales with the cross-linking density. As a result of stoichiometric imbalance, dangling/pendant chains are formed as well as a significant sol fraction, if the mixing ratio is moved far away from the recommended ratio.[51,92,120] Dangling chains and sol fractions introduce significant viscous loss and thereby lead to heat generation. Furthermore, the sol fraction behaves comparable to silicone oil and therefore acts as a plasticiser. Non-ideal cross-linking leads to soft and – when taken to the extreme – sticky and non-coherent elastomers.

As a summary of the preceding discussions, it is clear that no matter the utilised commercial silicone elastomer, they provide great reliability and are therefore ideal candidates for further elastomer optimisation. However, to exploit fully the potential of silicone-based dielectric elastomers a higher dielectric constant is required. The following sections deal with various methods for improving dielectric permittivity while maintaining the fundamentally favourable properties of the silicone elastomer matrix.

## 4. Silicone composites for dielectric elastomers

The traditional choice of fillers for silicones has been silica particles, because they interact well with the PDMS matrix. The fillers can either be blended directly into the elastomer precursor or be incorporated through in-situ condensation reactions during condensation curing.[121] For application in DETs there is a requirement for increased dielectric permittivity, in order to improve the actuation efficiency of systems. The addition of a filler of high permittivity to the elastomer system is one of the most investigated solutions to this challenge. However, as a result of the often relatively high silica content (30-40%) in most silicone systems, the choice to increase filler content comes at the cost of an inherent increase in the elastic modulus of the elastomer. This is a remarkable disadvantage for actuation, because the electromechanical strain resulting from the electrostatic pressure is inversely proportional to the elastic modulus of the

material.[122] For the optimal system a balance will have to be found between reinforcement and permittivity increase while not compromising the elastic modulus.

When designing a given formulation there are many considerations that need to be taken into account. In particular the interface between particles and the polymer matrix has been seen to influence greatly the effects of different types of fillers in polymer composites. Here especially, the use of derivatised particles facilitates improved dispersion as well as improved compatibility with the matrix.[123] In this context both the type of filler particle applied. e.g. $SiO_2$, $TiO_2$, $BaTiO_3$, affects not only the obtained properties, but also the handling of the particles, such as drying to prevent adsorbed moisture, as observed by Böse et al.[124] as well as Kofod et al.,[125,126] who recognised the great importance in preventing premature breakdown. In developing new systems, the prediction of properties from mixing rules based on the specifications of a given filler has been sought by applying a range of different models used for the theoretical prediction of dielectric permittivities.[127] Recently, it appears that examples such as the Yamada[128] or Bruggeman[129] models, applied more frequently throughout the literature, have been showing good correlations with experimental data. It is very clear from Table 2 to 6 that many different combinations of PDMS based elastomers, different sized nanoparticles and dispersion methods have been tested. The various systems have different advantages and dependencies, although a direct comparison is sometimes difficult, as there are many experimental differences in addition to the abovementioned considerations on filler material and surface derivatisation and compatibilisation. Local availability strongly affects the selection of particles, and it is difficult to conclude anything with respect to these parameters, though it appears to be a general trend that smaller particles provide an improved effect due to a larger surface area and improved distribution in the matrix.

The methods of choice for the mechanical dispersion of particles in silicone generally cover a broad range of methods, such as direct mechanical mixing at various shear strengths and in various laboratory mixers,[111,127,130–137] in-situ formation of particles,[121] ultra-sonication (US)

in combination with solvents,[111,138–142] ball milling,[143,144] three or two roll mills[145,146] and speedmixing.[147–149] Often it is noted that a combination of these methods or use of additional dispersion aids in the form of plasticisers or functionalised and/or stabilised particles gives the best results in terms of dispersion. From an industrial point of view many of these processes are only effective on a laboratory scale and would be challenging to implement in full-scale production. However, methods such as roll milling or speedmixing have been implemented and up-scaled for industrial production.

When considering the use of dispersing agents, plasticisers especially have been investigated in several systems,[127,133,138,144,150,151] where it has been seen that it is possible to ensure a better dispersion of the filler and a reduction in the Young's modulus of the samples. The addition of free plasticisers into the material introduces a mobile component in the formulation, which could be a problem for long-term stability. Generally, large amounts of mobile additives would be expected to give rise to long-term instabilities and losses in the material, as discussed previously. Therefore, the design of such systems requires a careful balance between the dispersion and stability of the cross-linked system.

In addition to the random orientation of the fillers, anisotropic orientations, in order to imprint specific properties into the material in the actuation direction, have also been investigated in recent years. This has either been obtained by electrical field orientation,[152] by use of magnetic fields for magnetic particles[153] or by dielectrophoresis (alignment due to a non-uniform electrical field).[123]

One of the most widely studied filler materials used for increasing dielectric permittivity in silicones is $TiO_2$, due to its high dielectric permittivity (rutile: $\varepsilon' = 114$, anatase: $\varepsilon' = 31$). The first group to report the use of $TiO_2$ as a dielectric constant-enhancing filler material was Carpi et al.,[127] who used mechanical mixing to disperse the $TiO_2$ in a three-component PDMS precursor using plasticiser. The approach afforded a cross-linked material with a dielectric permittivity of $\varepsilon' = 8$ at 30 phr of $TiO_2$. Many systems applying $TiO_2$ have subsequently been

investigated, and it is very often included as a reference material for comparing the properties of new composite candidates in more recent studies.[110,148] An overview of studies reporting applications of $TiO_2$ as a filler in silicone for DET applications can be seen in **Table 2**.

In addition to the work on $TiO_2$, several different inorganic particles with high dielectric permittivity have been investigated for use as fillers in silicones. Titanates of various kinds, such as $BaTiO_3$ (relative dielectric permittivity of $\varepsilon' = 6000$), copper calcium titanate ($CuCaTiO_3$, CCTO, relative dielectric permittivity of >3000), lead magnesium niobate ($(PbMg_{1/3}Nb_{2/3})O_3$, PMN, relative dielectric permittivity of $\varepsilon' = 4000$), lead magnesium niobate – lead titanate ($(PbMg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, PMN-PT, relative dielectric permittivity of $\varepsilon' = 4000$) and lead zirconia titanate ($PbZrTiO_3$, PZT, relative dielectric permittivity of $\varepsilon' = 1800$) have been investigated, and a summary of these systems has been compressed into **Table 3**. Generally speaking, silicones with $BaTiO_3$ provide similar dielectric permittivities (relative dielectric permittivities of $\varepsilon' = 5$-8) compared to the $TiO_2$ with a lower amount of added filler. However, Zhang et al.[150] reported the highest relative dielectric permittivity of $\varepsilon' = 300$ at 10 wt% $BaTiO_3$ with a dielectric loss of only $\tan\delta = 0.22$. This system, however, did employ 35% plasticiser, which might influence long-term stability. Of the other titanates the highest relative dielectric permittivity was reported by Yang et al.[146] for PMN with a relative dielectric permittivity of $\varepsilon' = 27.5$ at 60 vol% filler. However, they found that for actuating purposes a lower loading of 20 vol%, resulting in a dielectric permittivity of $\varepsilon' = 5.2$, was optimal. This resulted in a material with an actuation strain of 7.9% at 53 V/μm. A number of PZT PDMS composites have been evaluated for use in piezolectronics, showing highly increased permittivities of $\varepsilon' = 28$ with 40 vol% PZT[154] and $\varepsilon' = 160$ with 32.5 vol% PZT.[155] However, these specific systems have not yet been evaluated for their properties in DET systems with respect to actuation and breakdown properties. Other PMN-PT and PZT PDMS systems have been recently identified as some of the more promising candidates for applications in wave harvesting applications using dielectric elastomers due to their promising overall properties.[156]

In addition to inorganic fillers, several complexes with various metals in silicone have been investigated for DET applications. As an example, iron, cobalt and titanium complexes were investigated by Cazacu et al.,[157] who discovered dielectric permittivities of up to $\varepsilon' = 4.7$ with 3-5 wt% of the respective complexes. Also, copper-phthalocyanine (CPO) complexes have been investigated due to their high dielectric permittivity (>10.000), with Zhang et al.[100,158] showing a dielectric permittivity of $\varepsilon' = 5.85$ at 20 wt% CPO and improved actuation. The dielectric properties of the elastomers were later observed to be strongly influenced by the amount of adsorbed water, as reported by Opris et al.[159]

Based on the assumption that interfacial layers are driving factors behind increasing dielectric permittivity, several groups have used organo-clays incorporated into silicone to increase the respective dielectric permittivities. An overview of the silicone materials reported on the incorporation of clays can be seen in **Table 4**.

Generally either pristine clays, surfactant-modified MMT or specially modified clays have been investigated, resulting in dielectric permittivities from $\varepsilon' = 3.7$ and up to $\varepsilon' = 5.8$ with intermediate losses. In addition, reduced relaxation times were observed in one case by Gharavi et al.[132] The primary challenge observed has been the dispersion of the clays in the hydrophobic silicone matrix.

In an effort to increase permittivity, a range of conductive fillers such as conductive polymers, carbon black, multi-walled carbon nanotubes (MWCNTs) and exfoliated graphite have been investigated. The conductive fillers introduced into silicone for DET applications are summarised in **Table 5**.

Generally, the challenge with conductive fillers is preventing percolation and short-circuiting of the electroactive polymers. There are currently two approaches applied in the literature for the use of conductive materials in electroactive polymers. Either the loading of the conductive filler is kept below the percolation threshold or the conductive particles are encapsulated to prevent percolation in the case of higher conductive filler content.

Fillers loaded at levels below the percolation threshold permit loadings of 1-5 wt% for carbon black, generally up to 0.5 wt% for MWCNT and up to 4 wt% for expanded graphite, depending on the method of dispersion. The advantage of these approaches is the simplicity of adding the filler directly, but substantial loss has been observed in most of these cases which would be expected to give rise to substantial challenges in long-term stability. To circumvent these challenges Goswami et al.[149] introduced a more advanced mixing scheme to permit in-situ entrapment of MWCNT in silicone while maintaining controlled dispersion. By this approach the content of MWCNT could be increased by up to 1 wt% while still maintaining a non-conductive matrix. However, considerable leakage currents were observed at elevated temperatures and electrical breakdown was reduced to 20 V/μm at 1 wt% MWCNT.

In the area of conductive polymers both direct mixing and isolation from the matrix have been applied, with the direct blending of conductive polymers (which will be treated in the subsequent section). However, in order to apply these materials for DETs it is necessary to either go below the percolation threshold or to encapsulate the conductive polymer, as illustrated in **Figure 5**.

The encapsulation approach has been investigated by Opris et al. in several publications with divinylbenzene encapsulated polyaniline (PANI) particles (Figure 5 top left and middle). The authors[52,159] prepared both poly(styrenesulfonic acid)-stabilised PANI nanoparticles as well as poly(divinylbenzene) (PDVB)-encapsulated PANI particles, which after blending into a silicone matrix showed increased dielectric permittivity from $\varepsilon$' = 2.3 to almost 5 at low frequencies. Next, 15 vol% PANI in PDVB (13 wt% PANI in 87 wt% PDVB) in a silicone matrix created composites with improved electromechanical responses that reached 12% strain at 50 V/μm.[160] In a further development by Opris et al.[161] the silicone matrix was optimised using different condensation cure cross-linking chemistries to encompass the PDVB-PANI particles better. Using the optimised silicone matrix and 20 wt% PDVB-PANI particles good properties were obtained, such as increased dielectric permittivity, low dielectric loss, large

strain at break (>1000 %) and a lateral actuation strain of 12% at 40 V/μm for a 30% pre-strained film. A summary of the studies conducted on core-shell fillers can be seen in **Table 6**. As shown in Figure 5 (bottom), Yang et al.[162] similarly developed a system for encapsulating Ag particles by using a silica core covered with polydopamine, which was in a step-wise fashion covered with Ag particles immobilised on the surface. A subsequent polydopamine layer could be used to control the thickness of the isolating layer, and thereby the permittivity of the system, where an optimum level was found with a dopamine layer of 15 nm and a loading of up to 50 vol%, thus providing a dielectric permittivity of up to $\varepsilon' = 50$. Recently, Quinsaat et al.[163,164] have also shown how Ag particles covered by a $SiO_2$ shell could be used to obtain a permittivity of $\varepsilon' = 5.9$. As with other conductive fillers they observed a reduced dielectric breakdown strength of 13.4 V/μm, as also mentioned above for the other conductive fillers.

In addition to the systems mentioned above, there are also reports of the use of inorganic core-shell particles such as $SiO_2/TiO_2$ by Vudayagiri et al.,[147] or liquid core-shell particles enabling the use of liquid high-permittivity fillers such as the ionic liquids recently investigated by Mazurek et al.[165,166] In all cases the use of core-shell particles enables the employment of otherwise inaccessible fillers in dielectric elastomers, and it will be interesting to follow future developments within this area.

However, a very often ignored effect of hard fillers in the silicone elastomer is that the resulting elastomer composites experience severe stress-softening in cyclic experiments (Mullins softening), and they may experience mechanical ageing (fatigue) upon pre-straining,[65] which subsequently causes loss of tension and strain reversibility in the composites. Young's moduli have been shown to decrease by a factor of approximately two for silicone elastomers with 35 phr $TiO_2$ upon pre-straining at 120% for three months, whereas commercial silicone elastomers do not show the same tendency. Obviously, it is very important when formulating elastomers to maintain elasticity and stability in order to utilise the performance strengths of silicone elastomers, namely fast responses, large and reproducible strains and overall stability.

Commercial elastomers experience negligible ageing, thereby making them ideal candidates for DET products. With the right precautions, i.e. minimising filler content (of course with decreased permittivity as a trade-off) and limiting the amount of oils and solvents used in the preparation process, the favourable properties of commercial elastomers may be transferred successfully to composites.[65]

## 5. Silicone/polymer blends for dielectric elastomers

Alternatively, a very efficient method to increase effectively the electromechanical response of silicone elastomers involves blending in components such as polymers with high dielectric permittivity. Such polymers simultaneously decrease the Young's modulus and increase dielectric permittivity, thus increasing electromechanical responses significantly. Increasing the electromechanical response of a PDMS elastomer, for example, has been achieved by blending in small amounts (1-6 wt%) of the highly conjugated, un-doped poly(3-hexylthiophene) (PHT) with high values of $\varepsilon'$ (>2000 at 1 Hz).[167,168] Blend homogeneity was ensured by initially using liquid phases, PDMS in the pre-polymer stage and PHT as a chloroform solution, after which the silicone matrix was cured. In a blend with 6 wt% PHT low Young's modulus ($Y$ = 69 kPa) and high dielectric permittivity ($\varepsilon'$ = 13.8, at 1 Hz) were obtained. The system, however, suffered from high dielectric losses. A more optimal concentration of 1 wt% is therefore presented in **Table 7**.

Gallone et al.[169] used a PDMS/polyurethane blend comprised of a commercial three-component PDMS-based formulation (TC-5005 A/B-C by BJB Enterprises Inc.), a moisture-cure system which contains a PDMS-based plasticiser and a two-component polyurethane elastomer (poly 74 from Polytek Development). A blend prepared with 40 vol% polyurethane achieved dielectric permittivity ranging from $\varepsilon'$ = 5.2 at high frequencies (>1000 Hz) to $\varepsilon'$ = 15.5 at 10 Hz. Thus, permittivity was observed to be even higher than that of pure polyurethane ($\varepsilon'$ = 6.5 at low frequencies), which was ascribed to the Maxwell-Wagner-Sillars polarisation

of the interphases in the blend. An actuation strain of 2.7 % at 5.5 V/μm was achieved, but dielectric loss was significant and resulted in decreased dielectric breakdown strength.

In another type of blend two polyethylene glycols, with average molecular weights of 600 g $mol^{-1}$ (PEG600) and 1500 g $mol^{-1}$ (PEG1500), were blended with the liquid silicone Silastic DC3481.[170] In a blend with 5 phr PEG600, a dielectric constant of $\varepsilon' = 5.4$, a Young's modulus of 0.85 MPa and an actuation strain of 11.5% at 40 V/μm were achieved, the latter of which was 64% higher than pure PDMS. In order to overcome the immiscibility of PDMS and PEG, Razak et al.[171] prepared PEG-PDMS multi-block copolymers which were then blended into a commercial silicone elastomer (MJK 4/13 from Wacker Chemie). On a microscopic scale, such blends with low PEG-PDMS block copolymer concentrations were seen to create completely homogenous films, whereas at high concentrations, spherical domains of PEG were observed in the thin films. Using 5 wt% of the PEG-PDMS block copolymer, dielectric permittivity was found to increase by 60% while dielectric losses remained low and dielectric breakdown strength was maintained at approximately ~100 V/μm.

Risse et al.[172] prepared a blend of a ~2300 g $mol^{-1}$ cyanopropyl-functional PDMS and a PDMS matrix, where the cyano-functional PDMS acted both as a filler and as a plasticiser, as seen in **Figure 6**. Dielectric permittivity increased significantly (~two-fold), but this upturn was accompanied by a 75% decrease in electrical breakdown strength (from 80 V/μm to 20 V/μm). Commercial fluorosilicones were investigated early on by Pelrine et al.[50] but were shown to exhibit high leakage currents.[47] Later, Böse et al.[173] prepared a home-made system using trifluoropropyl-functional divinylpolydimethylsiloxane, cross-linked into an elastomer and mixed with fluorinated silicone oil, to create very soft silicone elastomers ($Y$ = 0.07 MPa at 45 wt% oil) with enhanced dielectric permittivity of up to $\varepsilon' = 5.4$. The actuation strain was improved by a factor of five using 40 or 45 wt% fluorinated silicone oil, though the leakage current was not stated.

In order to overcome the increased dielectric losses that usually arise when attempting to increase dielectric permittivity, Madsen et al.[174,175] used a chloropropyl-functional silicone oil, namely LMS-152 from Gelest Inc., as an additive to the commercial silicone elastomer LR3043/50, supplied by Wacker Chemie. At a content of up to 30 phr LMS-152 dielectric permittivity increased to $\varepsilon' = 4.4$ while the dielectric loss tangent decreased. Furthermore, LMS-152 proved to decrease the dielectric loss of a $TiO_2$-containing silicone elastomer. Thus, this study proved that it is possible to increase permittivity while not compromising dielectric loss, which is a positive step forward towards low-loss materials. Due to the softening effect of the chloropropyl-functional silicone oil, the Young's modulus of LR3043/50 decreased from 2 MPa to 1.35 MPa. This decrease in the Young's modulus, interestingly, did not decrease dielectric breakdown strength, which in fact increased from 121 V/μm to 130 V/μm. Thus, the addition of LMS-152 did not compromise any of the important DET properties, albeit the long-term stability of such materials still needs further investigation.

Silicone elastomer blends seem like an interesting and simple method for improving the electromechanical response of silicone-based DETs. However, as discussed for the silicone composites, ageing studies are required in order to evaluate the long-term stability and reliability of these blends. Moreover, free species (blended-in species) may migrate and cause changes in the elastomer structure over time.

## 6. Chemically modified silicones for dielectric elastomers

Another approach to silicone elastomers with increased DET performance is to chemically graft organic dipoles to the PDMS elastomer network. Molecules/chemical groups with high dipole moments increase the polarisability of the elastomer and thereby increase dielectric permittivity and energy density. This approach potentially leads to a more controlled network structure, as it does not rely on the efficient and perfect mixing of particles or blends. Furthermore, such

covalently grafted systems should provide a more stable elastomer system upon continued activation of the material.[110] Several interesting systems have been developed in this respect. Kussmaul et al.[176,177] and Risse et al.[178] added the synthesised dipolar molecule *N*-allyl-*N*-methyl-*p*-nitroaniline, together with compensating amounts of a hydride-functional cross-linker, to a PDMS matrix and a commercial silicone elastomer system, respectively, in one-step processes. Two-fold increases in dielectric permittivity were obtained compared to a silicone reference. However, the direct addition resulted in a competitive reaction with the network formation reaction, ultimately resulting in a high risk of network imperfections such as dangling substructures and large sol-fractions, which could be washed out of the network. Therefore, at high nitroaniline concentrations, significantly softer networks were obtained and electrical breakdown strengths were significantly reduced, as seen in **Table 8**.

As an alternative approach Racles et al.[179] developed a system in which cyanopropyl-groups were distributed along the backbone of PDMS chains. Cyanopropyl-functional hydroxyl-terminated PDMS was prepared through the ring-opening polymerisation of different cyclotetrasiloxanes. Silicone elastomers were then prepared by cross-linking reactions with ethyltriacetoxysilane and a titanium tetra(2-ethylhexoxide) catalyst. Dielectric permittivity was found to increase two-fold, but this increase in permittivity was followed by an increase in conductivity and poorer mechanical properties. Favourable results were obtained when mixtures of the cyanopropyl-functional PDMS and a PDMS pre-polymer were used to form elastomers[179] (Table 8). In a further development with cyanopropyl-functional materials,[180,181] (see **Figure 7**) a permittivity of $\varepsilon' = 4.5$ and a breakdown strength of 56 V/μm were achieved, while a 13-times higher actuation strain compared to silicone was also obtained.

In order to distribute functionality in a controlled manner, Madsen et al.[182–184] developed a new silicone-compatible azido-functional cross-linker that allowed for specific functionalisation with high dipole moment molecules at the cross-linking point of silicone networks. This was achieved by using a copper-catalysed azide-alkyne 1,3-dipolar

cycloaddition (CuAAC), which is orthogonal to the cross-linking reaction, so that functionality could be added without compromising the network-forming addition cure reaction. The advantage of this method was highly controlled functionalisation, whereby the dipolar groups (nitrobenzene and nitroazobenzene) were ensured to be very well distributed throughout the network, as the cross-linker allowed for only one functional group per cross-linker molecule, as seen in **Figure 8**. Consequently, the mechanical properties of the functionalised elastomer could be controlled and maintained easily. Since the functional groups were directly bound to the cross-linker, this also limited the maximum loading of the dipolar groups, leading to modest improvements in dielectric permittivity of up to 20%.

In order to increase the possible concentration of functional groups, Madsen et al.[185,186] developed a new method distributing the functional groups on the backbone of a copolymer instead of at the cross-linking points, thereby increasing the amount of functional groups drastically. Copolymers allowing for addition cure were synthesised through the tris(pentafluorophenyl)borane-catalysed Piers–Rubinsztajn reaction of 3-chloropropylmethyldimethoxysilane and hydride-terminated dimethylsiloxane pre-polymers of different lengths, in order to create copolymers with spatially well-distributed azido groups that allowed for further functionalisation with, for example, high dipole moment molecules via CuAAC, as seen in **Scheme 2**. This method allowed for complete control over the concentration and distribution of functional dipolar groups along the backbone of silicone polymers, and as a result the mechanical properties could be easily tuned to produce high breakdown strengths. The system, however, at high functional dipolar nitrobenzene group concentrations, suffered from high dielectric losses at low frequencies and slightly increased conductivities.

Bele et al.[187] used an approach similar to that employed by Madsen et al.,[182] by using functional cross-linkers to increase the dielectric permittivity of silicone elastomers. The cross-linkers consisted of commercial R-trialkoxysilanes which were cross-linked with polydimethylsiloxane-α,ω-diols in condensation cure reactions, using dibutyltindilaurate as a

catalyst. Although somewhat higher electromechanical actuation was achieved, this method did not increase $\varepsilon'$ significantly and led to increased moisture sorption values. No conductivity or dielectric breakdown values were presented.

Dünki et al.[188,189] functionalised a high molecular weight hydroxyl-terminated polymethylvinylsiloxane with 3-mercaptopropionitrile, which were cross-linked using 2,2′-(ethylenedioxy)diethanethiol – a bi-functional thiol. High dielectric permittivity ($\varepsilon'$ = 10 at 1 MHz) and a large actuation strain (20.5% at 10.8 V/μm) were obtained. However, dielectric losses (tan $\delta$ > 1) and conductivity increased significantly at low frequencies, while dielectric breakdown strength was very low (10.8 V/μm). A major advantage of this material, nonetheless, was that it experienced self-healing properties upon dielectric breakdown, which is a strongly desired ability for augmenting the lifetime of DETs.

Zhang et al.[190] created high permittivity silicone elastomers, with a functionalisation approach similar to that used by Kussmaul et al.,[176] using a dihydroxyl-functional nitroazobenzene dipolar molecule in a condensation reaction with hydroxyl-terminated PDMS, a tetraethylorthosilicate cross-linker and a dibutyltin dilaurate catalyst. However, in this study a *difunctional* dipolar molecule was used in condensation reactions, and therefore it could actively participate in the curing process (as chain extender/additional cross-linking site) and would not just block one of the cross-linking sites (see **Figure 9**). Consequently, the network-forming reaction was not compromised to the same extent as in the work of Kussmaul et al.[176] The dielectric constant was found to increase in line with increasing nitroazobenzene content, reaching $\varepsilon'$ = 4.9 at 1 KHz. Stress-strain measurements revealed an increasing Young's modulus and elongation at the breaking point in line with increasing nitroazobenzene content, attributed to increased cross-linking density. Dielectric breakdown strength was found to increase to 89.4 V/μm at low concentrations (4 wt% nitroazobenzene), and thereafter it decreased in line with increasing content, reaching 56.7 V/μm at 13.2 wt%. A maximum actuation strain of 17% at ~68 V/μm was obtained for a sample containing 7.1 wt% nitroazobenzene, which also

showed the highest value of electromechanical sensitivity ($\varepsilon'/Y$). Dielectric losses, however, were not presented.

Recently, a very promising and much simpler silicone elastomer system, based on chloropropyl-functional siloxane copolymers, has been developed by Madsen et al.[174,191] These elastomers possessed a low Young's modulus (0.4 – 1 MPa, 75-90% lower than the utilised silicone reference) and high dielectric permittivity ($\varepsilon'$ = 4.7 at 1 MHz). Dielectric losses, remarkably, remained as low as those of pure PDMS elastomers, and high dielectric breakdown strengths were obtained (94.4 V/μm), thus increasing the maximum achievable actuation, $\varepsilon'/Y \cdot E_B^2$, significantly (between seven and ten times). Furthermore, the gel fractions and viscous losses remained in the same order of magnitude as a PDMS reference elastomer, and so the softness of the system did not compromise material stability.

In summary, chemical modifications made to silicone elastomers, in order to increase dielectric permittivity and/or electromechanical response, frequently lead to a compromise in properties. At high concentrations of functional groups, high dielectric permittivities are obtained. This, however, is often accompanied by an increase in dielectric loss or a significant decrease in dielectric breakdown strength. In the design of such systems it is therefore very important to keep in mind and investigate these properties, as they all greatly influence the lifetime and stability of the silicone DET. On the other hand, such modified systems will most likely be more stable and reliable over time and less prone to ageing effects than blends or silicones heavily filled with metal oxides.

## 7. Systems with complex network structures for dielectric elastomers – interpenetrating and bimodal networks

A different approach to improving silicone elastomers involves altering the network structure by, for example, creating interpenetrating polymer networks (INPs) or bimodal networks.

An IPN is a network that consists of two or more polymers that are cross-linked in-situ, to produce interlaced networks. IPNs have different and often superior properties compared to the

respective homo-polymers, which is due to stabilised bulk and surface morphologies created by the interlaced networks. There are two main routes used to prepare IPNs (**Figure 10**): either sequentially or simultaneously. In the sequential method, the IPN is formed in two consecutive steps, where initially a homo-network of polymer(I) is formed through cross-linking. This network is then swollen with monomer or polymer(II), cross-linker and an initiator, and the IPN is formed through in-situ polymerisation or cross-linking. The second method consists of forming two independent networks simultaneously. This is done by either cross-linking two sets of polymers or through polymerisation and cross-linking two monomers through non-interfering orthogonal reactions.[192,193]

For many years the main focus of IPNs as dielectric elastomer actuators was on highly pre-strained acrylic 3M VHB tape, due to this material's high dielectric breakdown strength and large strains. The VHB IPN is created via a sequential approach by treating the pre-strained acrylic VHB film with a cross-linkable monomer and an initiator and then allowing the monomer and initiator to diffuse into the film. The monomer, upon thermal curing, forms a second polymer network, interlaced with the acrylic network. The formed IPN is allowed to relax to zero stress, which makes the acrylic network contract and the second network compress.[194–196] The two interpenetrating networks are now in equilibrium, with one network highly stressed and the other highly compressed. The additive network works as a support for the pre-strained acrylic network, thus eliminating external pre-strain supporting structures. These IPNs, however, have poor frequency responses and are very temperature and moisture sensitive, due to their acrylic nature.

In order to exploit some of the advantageous properties of silicones, such as their broad temperature operating range, low moisture absorption and lower tensile modulus, Mathew et al.[197] combined VHB acrylic elastomers with a silicone-based elastomer. The silicone chains were swollen with a co-solvent into the acrylic film and subsequently cross-linked. The resultant IPN material was shown to possess properties between the properties of the homo-

networks, thus improving some important properties of the acrylic elastomer. This included greater tensile strength, which was believed to be due to the reinforcing silicone network which represented constraining points during the deformation of the acrylic network, and a Maxwell stress higher than that obtained by pure acrylic elastomer at similar voltage levels.

Limited literature has been published regarding the use of non-acrylic-based IPNs as dielectric elastomers; however, Brochu et al.[63] prepared an all-silicone-based IPN using a soft room temperature vulcanising (RTV) (Dow Corning HSIII) silicone, which served as a host elastomer matrix, and a rigid high temperature vulcanising (HTV) (Elastosil LR3003/70) silicone, which was used to preserve pre-straining in the host elastomer. The IPN was prepared by mixing the two liquid silicones in a co-solvent and drop-casting the mixture on a poly(styrene sulfonate)-treated glass. The RTV Dow Corning HSIII silicone, based on silanol-terminated PDMS, a tetrapropyl orthosilicate cross-linker and a dimethyl tin di-neodecyl ester catalyst were then allowed to cure at RT, and the resulting film was then peeled from the substrate and pre-strained bi-axially. The HTV Elastosil LR3003/70 silicone, based on addition cure components, was then cured at 180°C. The prepared materials showed increasing stiffness in line with increasing HTV Elastosil silicone concentration, and therefore it also showed increased dielectric breakdown strength in line with increasing content. Furthermore, the prepared materials had higher achievable actuation strains of 25% at 55 V/μm, which was 100% more than the homo-polymer alone. An additional advantage of the method was that the electrode materials could be bonded strongly to the surface layer of the silicone by applying the electrode material before curing the HTV silicone.

Building on the procedure set out by Brochu et al.,[63] Tugui et al.[198] also used an interpenetrating silicone system of addition and moisture cure components to lock-in pre-strain. The difference in this work was the molecular weight of the chosen components, giving the network bimodality. The vinyl-cure polymer ($\bar{M}_n$= 34,500 g mol$^{-1}$) had a molecular weight ten times lower than that of the moisture cure polymer ($\bar{M}_n$= 370,000 g mol$^{-1}$). The resulting IPNs

had increased breakdown strength compared to their un-stretched IPN counterparts, and similar to the findings of Brochu et al.,[63] breakdown strength increased in line with increasing content of the addition cure network. The study, however, found that while the actuation strain increases in line with increasing content of the addition cure network, it decreases when pre-straining of one of the networks is applied. The authors concluded that bimodality seems to be more significant for the actuation strain than the pre-straining facilitated by the IPN structure. The data presented in **Table 9** are therefore for an IPN prepared with no pre-straining.

IPNs composed of ionic networks with very high dielectric permittivities[199,200] and conventional silicone elastomers in various ratios constitute a novel class of dielectric elastomer. In the most recent development, cross-linked ammonium carboxylates were prepared by blending carboxydecyl-terminated PDMS (DMS-B15 or DMS-B25 from Gelest Inc.) and aminopropylmethylsiloxane dimethylsiloxane copolymer with, on average, four amino groups per chain (AMS-162).[201,202] Blends of these ionic networks and commercial silicone elastomers, such as Elastosil RT625 (RTV), Powersil XLR630 (LSR) and Elastosil LR3043/30 (LSR), created a range of high-energy density interpenetrating networks. Good overall properties stemmed from the softening effect and very high permittivity of ionic networks – as high as $\varepsilon' = 7500$ at 0.1 Hz – while the silicone elastomer part of the IPN provided mechanical integrity as well as relatively high breakdown strength (around 90 V/μm). When all of these parameters were compared to a commercial silicone elastomer in figure of merit calculations for both actuator and generator applications, the IPNs prepared particularly with LR3043/30 performed exceedingly better than the silicone reference at the lowest frequencies, albeit with moderately better behaviour at the high frequencies only. Another interesting feature of these IPNs was their self-healing properties, which allow broken materials that have suffered dielectric breakdown to be repaired after moderate heating for a few hours.[201,202]

Bimodal networks, which consist of a mixture of very short and relatively long chemically identical polymer chains, can be used as a tool to improve the mechanical properties of silicone networks.[203,204] Several studies have investigated the unexpected high tear and ultimate strength of bimodal networks.[205–207] The elastic modulus of these bimodal networks increases significantly at high elongations, and consequently the ultimate strength of these silicone networks is very high. Improvements in ultimate strength stem from the limited extensibility of the short chains, which gives the networks toughness.[208,209] Furthermore, these relatively long chains retard the rupture process and are responsible for the extensibility of the network.[207] Therefore, bimodal networks exhibit both significant ultimate stress and major ultimate strain.[204] Bimodal networks can be created with a random distribution of short polymer chains within the long chains (homogeneous bimodal networks)[204,210–212] or as heavily cross-linked short chain clusters joined to the long chain network (heterogeneous bimodal networks).[213–215] Bejenariu et al.[215,216] prepared both homogenous and heterogeneous bimodal networks and evaluated them as candidates for dielectric elastomers. The heterogeneous bimodal networks exhibited improved mechanical properties for DETs, such as a lower elastic modulus, which made them very soft and extensible, without compromising other properties such as network stability and viscous loss – something that is very difficult to obtain by using traditional monomodal networks. Madsen et al.[217] developed a novel visualisation tool which allowed the small-chain domains in heterogeneous bimodal networks to be characterised according to their size and distribution, and then they correlated this to their mechanical properties. This led to a multi-domain theory which suggested that effective cross-linking density is lower around the small-chain domains than in the bulk network, as seen in **Figure 11**. Small-chain domains therefore create a local softening effect in bimodal silicone networks, while the networks are still perfectly cross-linked due to a high number of reactive groups on the surface of the small-chain domains. These networks will consequently be softer and have a lower elastic modulus and lower viscous loss than mono-modal networks despite higher average cross-linking density.

This theory could possibly explain the interesting and non-contrary relationship between modulus and viscous loss exhibited by heterogeneous bimodal networks.

Goswami et al.[115,149] used heterogeneous bimodal networks as a means of incorporating percolative amounts of multi-walled carbon nanotubes (MWCNT) into thiolene-cured silicone elastomers. The elastomer composites were designed to contain amounts of MWCNT above the percolation threshold, without becoming conductive. This was done by adding the MWCNTs inside the small chain domains, which thus acted as macromolecular insulating shells around MWCNT clusters, as seen in **Figure 12**. Dielectric spectroscopy measurements showed an increase in dielectric permittivity in line with increasing MWCNT content, reaching $\varepsilon'$ = 4.7 at 1 wt% MWCNT, as well as the desired frequency-dependent conductivity for all samples. Furthermore, dielectric losses remained low. The composites showed moderate dielectric breakdown strength of 48 V/μm at 0.33 wt% MWCNT, which decreased to 20 V/μm at 1 wt%. This decreasing breakdown strength was explained by increased conductivity at elevated temperatures, due to sample heating at high MWCNT loading.

Since the emergence of synthetic elastomers, the structure-property relationship has been heavily investigated. Silicone elastomers from hydrosilylation reactions have been denoted as a so-called 'model elastomer system', as side reactions are limited and the reaction can be controlled easily by both temperature and inhibitors.[218] An understanding of cross-linking density, combined with various interactions arising when the silicone elastomer is filled with silica, is crucial for designing elastomers with specific mechanical properties. The filler addition is – as discussed earlier – vital for strength and elongation, as silicone elastomers with no fillers are usually too brittle or too soft to provide stable mechanical properties (depending on polymer chain length). However, altering the structure of the elastomer, such as by creating bimodal elastomers, may render fillers obsolete and open up the way for very soft, elastic elastomers with reliable elastomer properties. Further research into this notion may lead to

increased actuation, as softness can be introduced without increased viscous and dielectric losses.[217]

Also very recently, Goff et al.[219] presented work on a hetero-bifunctional chain extender leading to infinitely long PDMS chains with superior elasticity and without the waxy consistency of traditional high-molecular weight silicone. Yet another recent publication also proves that the effect of entanglements could be avoided by grafting side chains to the PDMS backbone.[220] These findings open up the opportunity to rethink the design of silicone elastomers, as both methods produce stable silicone elastomers with very low elastic moduli.

Additionally, the field of IPN is still relatively unexplored in relation to elastomers for dielectric elastomers, where the main focus up to now has been on utilising IPNs to lock in pre-strain. Further exploration into this type of elastomer may also lead to the discovery of better elastomers with favourable features, such as the possibility of locking in pre-strain in a commercially feasible way and adding self-healing properties to the elastomer.

## 8. Summary and conclusion

Silicone elastomers provide the basis for fast and reliable actuation. Commercially available elastomers that have been tested as DETs have shown great promise, with respect to both actuation and reliability, but they still suffer from being designed originally for other applications. In particular, the dielectric permittivities of commercial silicone elastomers still remain too low for most practical DET applications, due to high driving voltages. The simplest approach to increase dielectric permittivity is to add high dielectric permittivity fillers. The advantage of this approach is in particular the easy preparation as well as the large variety of fillers available from a large number of suppliers. Highly efficient mixing methods are essential tools in obtaining high-quality elastomers. Moreover, methods such as roll-milling or speedmixing seem to be the most promising approaches for an industrial application to be implemented and up-scaled for industrial production. For filled systems it is essential to strike

a balance between increases in permittivity, only a limited increase in Young's moduli, good film-forming properties, tear strength, process ability as well as long-term stability. In particular, stability needs to be tested fully for the most promising composite systems, in order to determine the optimal level of loading. Alternatively, other reinforcing approaches should be considered, thereby enabling a higher level of fillers, as seen in heterogeneous bimodal systems, for instance.

The formation of blends constitutes yet another facile method for improving the electromechanical response of DETs. The advantage of this method includes ease of fabrication, which could make the method directly applicable in the large-scale manufacture of dielectric elastomers. The obvious disadvantages of blending in components in silicone matrices include potential poor compatibility between the silicone matrix and the polymer filler, which can lead to unwanted phase-separation. If a silicone-like polymer filler is used, compatibility issues may be overcome, but long-term material stability due to migration might still be a major issue, since mechanical and/or dielectric properties are likely to change drastically over time. Therefore, ageing studies on such blends are of the utmost importance.

To ensure long-term stability, chemically modified silicones, such as grafted silicone elastomers with high dielectric permittivity, should be considered. Such systems have long-term stability due to a lesser tendency to exhibit Mullins effects as well as improved mechanical properties such as a lower Young's modulus and increased stress at breaking compared to composite systems. Chemically modified systems, however, often suffer from increased dielectric losses due to dipole relaxation mechanisms and Maxwell-Wagner-Sillars polarisation. This may in turn lead to reduced dielectric breakdown strengths, and therefore care must be taken to keep dielectric losses to reasonable levels. Furthermore, some types of chemical groups may inhibit cross-linking (whether addition or condensation cure), and so proper cross-linking of the elastomer must be ensured via an investigation of either sol fractions, through extraction experiments, or by measuring viscous losses.

In all of the above approaches focusing on improved dielectric permittivity, it is essential to consider the systems holistically and ensure network integrity and stability. The network structure can be used as a means of improved actuation through a controlled Young's modulus as well as to maintain low viscous losses. Bimodal networks can be used if soft and stretchable elastomers are desired, whereas IPNs make it possible to create free-standing films with pre-strain within the elastomer, without the need for support structures. The major disadvantage of these systems is their complexity, since their curing reactions are expanded to several steps.

## 9. Perspective

Even though several challenges still exist on the road toward commercialising DETs, they nevertheless hold great promise for future applications due to their unique properties, such as being lightweight, capable of large strains and of relatively low cost compared to similar technologies. Due to the complexity of dielectric elastomers there may be many paths toward improved materials. Both tuning the stress-strain response of the elastomers and increasing energy density via dielectric permittivity, or through combinations of the techniques discussed herein, may be suitable approaches. Too strong a focus on increasing dielectric permittivity or actuation strain, however, may not be the most optimal way to proceed forward, since there needs to be a greater emphasis on DETs as a whole because the lifetime of silicone elastomers with high permittivity or increased actuation strain may still be very poor. Therefore, a complete standardised characterisation of materials is essential for the proper evaluation of new elastomer candidates for DETs, following for example the standards recently proposed by the European Scientific Network for Artificial Muscles (ESNAM).[221] Lifetime is a key aspect in the further improvement of DETs, and it is vital for the potential commercialisation of the technology. A potential way to obtain higher lifetimes is by introducing self-healing capabilities into both elastomers[188,201] and electrodes,[222] as seen recently. It will be interesting to follow the

developments of self-healing materials for DETs and how this will affect materials research and especially future DET products.

## Abbreviations and symbols

| | |
|---|---|
| CCTO | $CuCaTiO_3$, copper calcium titanate |
| CPO | copper-phthalocyanine |
| CuAAC | copper(I)-catalysed azide-alkyne cycloaddition |
| $d$ | thickness of elastomer |
| DC | direct current |
| DET | dielectric elastomer transducer |
| $\varepsilon$' | dielectric permittivity |
| $\varepsilon$'' | dielectric loss |
| $\varepsilon_r$ | relative dielectric permittivity |
| $\varepsilon_0$ | vacuum permittivity |
| EAP | electroactive polymer |
| $E_B$ | dielectric breakdown strength |
| EMI | electromechanical instability |
| $f$ | cross-linker functionality |
| $F$ | frequency |
| $F_c$ | critical frequency |
| $F_{om}$ | figure of merit |
| φ | strain energy function |
| $G^*$ | complex shear modulus |
| $G$' | storage modulus |
| $G$'' | loss modulus |
| HCR | high consistency silicone rubber |
| HMDS | hexamethyldisilazane |
| HTV | high temperature vulcanising |
| IPN | interpenetrating polymer network |
| $\lambda$ | strain |
| LR | liquid rubber |
| LSR | liquid silicone rubber |
| ν | Poisson's ratio |
| MMT | montmorillonite |
| $\bar{M}_w$ | weight average molecular weight |
| MWCNT | multi walled carbon nanotube |
| $\mu$ | dipole moment |
| $\omega$ | frequency |
| $\omega_c$ | critical frequency |
| PANI | polyaniline |
| PDA | polydopamine |
| PDMS | polydimethylsiloxane |
| PDVB | polydivinyl benzene |
| $P_{el}$ | electrostatic pressure |
| PEG | polyethylene glycol |
| phr | parts per hundred rubber |
| PHT | poly(3-hexylthiophene) |
| PMN | $(PbMg_{1/3}Nb_{2/3})O_3$, lead magnesium niobate |
| PMN-PT | $(PbMg_{1/3}Nb_{2/3})O_3 - PbTiO_3$, lead magnesium niobate – lead titanate |
| PU | polyurethane |
| PZT | $PbZrTiO_3$, lead zirconia titanate |
| $r$ | stoichiometric imbalance/ratio |
| $r_c$ | stoichiometric imbalance/ratio for critical gelation |

| | |
|---|---|
| RT | room temperature |
| RTV | room temperature vulcanising |
| σ | conductivity |
| *s* | thickness strain |
| SC | space charge |
| SDBS | sodium dodecyl benzene sulfonate |
| SEM | scanning electron microscopy |
| Tan δ | loss tangent |
| THF | tetrahydrofuran |
| *U* | voltage |
| US | ultra-sonication |
| wt% | weight percent |
| *Y* | Young's modulus |

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[1] Y. Bar-Cohen, *Electroactive Polymer (EAP) Actuators as Artificial Muscles: Reality, Potential, and Challenges*, SPIE Press, Bellingham, Washington USA, **2004**.

[2] R. Pelrine, R. Kornbluh, J. Joseph, R. Heydt, Q. Pei, S. Chiba, *Mater. Sci. Eng. C* **2000**, *11*, 89–100.

[3] R. Kornbluh, R. Pelrine, Q. Pei, R. Heydt, S. Stanford, S. Oh, J. Eckerle, *Proc. SPIE* **2002**, *4698*, 254–270.

[4] P. Brochu, Q. Pei, *Macromol. Rapid Commun.* **2010**, *31*, 10–36.

[5] F. Carpi, S. Bauer, D. De Rossi, *Science* **2010**, *330*, 1759–1761.

[6] E. W. H. Jager, E. Smela, O. Inganäs, *Science* **2000**, *290*, 1540–1545.

[7] E. W. H. Jager, O. Inganäs, I. Lundström, *Science* **2000**, *288*, 2335–2338.

[8] S. A. Wilson, R. P. J. Jourdain, Q. Zhang, R. A. Dorey, C. R. Bowen, M. Willander, Q. U. Wahab, M. Willander, S. M. Al-hilli, O. Nur, et al., *Mater. Sci. Eng. R Reports* **2007**, *56*, 1–129.

[9] J. D. W. Madden, N. A. Vandesteeg, P. A. Anquetil, P. G. A. Madden, A. Takshi, R. Z. Pytel, S. R. Lafontaine, P. A. Wieringa, I. W. Hunter, *IEEE J. Ocean. Eng.* **2004**, *29*, 706–728.

[10] A. S. Shaplov, D. O. Ponkratov, P. S. Vlasov, E. I. Lozinskaya, L. V. Gumileva, C. Surcin, M. Morcrette, M. Armand, P.-H. Aubert, F. Vidal, et al., *J. Mater. Chem. A* **2015**, *3*, 2188–2198.

[11] Y. Bar-Cohen, *Artificial Muscles Using Electroactive Polymers (EAP): Capabilities, Challenges and Potential*, Jet Propulsion Laboratory, National Aeronautics And Space Administration, Pasedena, CA, **2005**.

[12] I. Graz, M. Kaltenbrunner, C. Keplinger, R. Schwödiauer, S. Bauer, S. P. Lacour, S. Wagner, *Appl. Phys. Lett.* **2006**, *89*, 073501.

[13] R. Schwödiauer, I. Graz, M. Kaltenbrunner, C. Keplinger, P. Bartu, G. Buchberger, C. Ortwein, S. Bauer, *Proc. SPIE* **2008**, *6928*, 69270Q–1–69270Q–10.

[14] M. Krause, I. Graz, S. Bauer-Gogonea, S. Bauer, B. Ploss, M. Zirkl, B. Stadlober, U. Helbig, *Ferroelectrics* **2011**, *419*, 23–27.

[15] Y. Wang, C. Sun, E. Zhou, J. Su, *Smart Mater. Struct.* **2004**, *13*, 1407–1413.

[16] J. D. W. Madden, in *Dielectr. Elastomers as Electromechanical Transducers* (Eds.: F. Carpi, D. De Rossi, R. Kornbluh, R. Pelrine, P. Sommer-Larsen), Elsevier Science, Amsterdam, **2008**, pp. 13–21.

[17] R. Pelrine, R. Kornbluh, G. Kofod, *Adv. Mater.* **2000**, *12*, 1223–1225.

[18] I. M. Graz, D. P. J. Cotton, S. P. Lacour, *Appl. Phys. Lett.* **2009**, *94*, 071902.

[19] L. Bay, K. West, P. Sommer-Larsen, S. Skaarup, M. Benslimane, *Adv. Mater.* **2003**, *15*, 310–313.

[20] S. Rosset, H. R. Shea, *Appl. Phys. A Mater. Sci. Process.* **2013**, *110*, 281–307.

[21] G. Kofod, Dielectric Elastomer Actuators, Technical University of Denmark, PhD Thesis, **2001**.

[22] T. G. McKay, B. M. O'Brien, E. P. Calius, I. A. Anderson, *Appl. Phys. Lett.* **2011**, *98*, 142903.

[23] C. Jean-Mistral, S. Basrour, J.-J. Chaillout, *Smart Mater. Struct.* **2010**, *19*, 085012.

[24] R. Pelrine, R. Kornbluh, J. Eckerle, P. Jeuck, S. Oh, Q. Pei, S. Stanford, *Proc. SPIE* **2001**, *4329*, 148–156.

[25] R. Heydt, R. Kornbluh, J. Eckerle, R. Pelrine, *Proc. SPIE* **2006**, *6168*, 61681M–1.

[26] R. Sarban, Active Vibration Control Using DEAP Transducers, University of Southern Denmark, PhD Thesis, **2011**.

[27] G. Kovacs, L. Düring, S. Michel, G. Terrasi, *Sensors Actuators, A Phys.* **2009**, *155*, 299–307.

[28] F. Carpi, A. Migliore, G. Serra, D. De Rossi, *Smart Mater. Struct.* **2005**, *14*, 1210–1216.

[29] Q. Pei, M. Rosenthal, S. Stanford, H. Prahlad, R. Pelrine, *Smart Mater. Struct.* **2004**, *13*, N86–N92.

[30] R. Pelrine, P. Sommer-Larsen, R. Kornbluh, R. Heydt, G. Kofod, Q. Pei, *Proc. SPIE* **2001**, *4329*, 335–349.

[31] R. Pelrine, R. Kornbluh, Q. Pei, S. Stanford, S. Oh, J. Eckerle, R. Full, M. Rosenthal, K. Meijer, *Proc. SPIE* **2002**, *4695*, 126–137.

[32] G. Kovacs, P. Lochmatter, M. Wissler, *Smart Mater. Struct.* **2007**, *16*, S306–S317.

[33] I. A. Anderson, T. A. Gisby, T. G. McKay, B. M. O'Brien, E. P. Calius, *J. Appl. Phys.* **2012**, *112*, 041101.

[34] Z. Yu, W. Yuan, P. Brochu, B. Chen, Z. Liu, Q. Pei, *Appl. Phys. Lett.* **2009**, *95*, 192904.

[35] R. Heydt, S. Chhokar, *Proc. Intl. Disp. Res. Conf.* **2013**, *5*, P7.

[36] P. Chakraborti, H. A. Karahan Toprakci, P. Yang, N. Di Spigna, P. Franzon, T. Ghosh, *Sensors Actuators, A Phys.* **2012**, *179*, 151–157.

[37] L. Maffli, S. Rosset, M. Ghilardi, F. Carpi, H. Shea, *Adv. Funct. Mater.* **2015**, *25*, 1656–1665.

[38] D. Xu, T. G. McKay, S. Michel, I. A. Anderson, *Proc. SPIE* **2014**, *9056*, 90561A.

[39] R. Sarban, R. W. Jones, E. Rustighi, B. R. Mace, *J. Syst. Des. Dyn.* **2011**, *5*, 643–652.

[40] C. Jordi, S. Michel, E. Fink, *Bioinspir. Biomim.* **2010**, *5*, 026007.

[41] R. Kornbluh, J. Eckerle, B. McCoy, "http://spie.org/x48868.xml," **2015**.

[42] C. Löwe, X. Zhang, G. Kovacs, *Adv. Eng. Mater.* **2005**, *7*, 361–367.

[43] R. Kornbluh, A. Wong-Foy, R. Pelrine, H. Prahlad, B. McCoy, *Mater. Res. Soc. Symp. Proc.* **2010**, *1271*, 1–13.

[44] S. Rosset, M. Niklaus, P. Dubois, H. R. Shea, *J. Microelectromech. Syst.* **2009**, *18*, 1300–1308.

[45] R. Shankar, T. K. Ghosh, R. J. Spontak, *Soft Matter* **2007**, *3*, 1116.

[46] A. O'Halloran, F. O'Malley, P. McHugh, *J. Appl. Phys.* **2008**, *104*, 071101.

[47] J. Biggs, K. Danielmeier, J. Hitzbleck, J. Krause, T. Kridl, S. Nowak, E. Orselli, X. Quan, D. Schapeler, W. Sutherland, et al., *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 2–15.

[48] R. D. Kornbluh, R. Pelrine, H. Prahlad, A. Wong-Foy, B. McCoy, S. Kim, J. Eckerle, T. Low, *MRS Bull.* **2012**, *37*, 246–253.

[49] L. J. Romasanta, M. A. Lopez-Manchado, R. Verdejo, *Prog. Polym. Sci.* **2015**, http://dx.doi.org/doi:10.1016/j.progpolymsci.2015.

[50] R. E. Pelrine, R. D. Kornbluh, J. P. Joseph, *Sensors Actuators A Phys.* **1998**, *64*, 77–85.

[51] A. L. Larsen, K. Hansen, P. Sommer-Larsen, O. Hassager, A. Bach, S. Ndoni, M. Jørgensen, *Macromolecules* **2003**, *36*, 10063–10070.

[52] M. Molberg, Y. Leterrier, C. J. G. Plummer, C. Walder, C. Löwe, D. M. Opris, F. A. Nüesch, S. Bauer, J.-A. E. Månson, *J. Appl. Phys.* **2009**, *106*, 054112.

[53] S. J. A. Koh, T. Li, J. Zhou, X. Zhao, W. Hong, J. Zhu, Z. Suo, *J. Polym. Sci. Part B Polym. Phys.* **2011**, *49*, 504–515.

[54] E. M. Arruda, M. C. Boyce, *J. Mech. Phys. Solids* **1993**, *41*, 389–412.

[55] J. S. Bergström, M. C. Boyce, *Macromolecules* **2001**, *34*, 614–626.

[56] A. Tröls, A. Kogler, R. Baumgartner, R. Kaltseis, C. Keplinger, R. Schwödiauer, I. Graz, S. Bauer, *Smart Mater. Struct.* **2013**, *22*, 104012.

[57] S. Zakaria, P. H. F. Morshuis, M. Y. Benslimane, L. Yu, A. L. Skov, *Smart Mater. Struct.* **2015**, *24*, 55009.

[58] D. Gatti, H. Haus, M. Matysek, B. Frohnapfel, C. Tropea, H. F. Schlaak, *Appl. Phys. Lett.* **2014**, *104*, 052905.

[59] Y. Sun, S. A. Boggs, R. Ramprasad, *Appl. Phys. Lett.* **2012**, *101*, 132906.

[60] L. Yu, A. L. Skov, *Unpublished* **2015**.

[61] S. Zakaria, P. H. F. Morshuis, M. Y. Benslimane, K. V. Gernaey, A. L. Skov, *Proc. SPIE* **2014**, *9056*, 90562V.

[62] R. Pelrine, R. Kornbluh, Q. Pei, J. Joseph, *Science* **2000**, *287*, 836–839.

[63] P. Brochu, H. Stoyanov, X. Niu, Q. Pei, *Smart Mater. Struct.* **2013**, *22*, 055022.

[64] S. Akbari, S. Rosset, H. R. Shea, *Appl. Phys. Lett.* **2013**, *102*, 071906.

[65] S. Zakaria, L. Yu, G. Kofod, A. L. Skov, *Mater. Today Commun.* **2015**, *4*, 204–213.

[66] X. Zhao, W. Hong, Z. Suo, *Phys. Rev. B* **2007**, *76*, 134113.

[67] M. T. Connor, S. Roy, T. A. Ezquerra, F. J. Baltá Calleja, *Phys. Rev. B* **1998**, *57*, 2286–2294.

[68] S. Vudayagiri, L. Yu, S. S. Hassouneh, U. Hansen, A. L. Skov, *Polym. Plast. Technol. Eng.* **2015**, *54*, 425–432.

[69] S. Vudayagiri, A. L. Skov, *Polym. Adv. Technol.* **2014**, *25*, 249–257.

[70] S. Vudayagiri, M. D. Junker, A. L. Skov, *Polym. J.* **2013**, *45*, 871–878.

[71] P. Sommer-Larsen, A. L. Larsen, *Proc. SPIE* **2004**, *5385*, 68–77.

[72] T. G. McKay, E. Calius, I. A. Anderson, *Proc. SPIE* **2009**, *7287*, 72870P–1–72870P–10.

[73] R. D. Kornbluh, R. Pelrine, J. Joseph, R. Heydt, Q. Pei, S. Chiba, *Proc. SPIE* **1999**, *3669*, 149–161.

[74] J. Zhou, W. Hong, X. Zhao, Z. Zhang, Z. Suo, *Int. J. Solids Struct.* **2008**, *45*, 3739–3750.

[75] M. Moscardo, X. Zhao, Z. Suo, Y. Lapusta, *J. Appl. Phys.* **2008**, *104*, 093503.

[76] J. S. Plante, S. Dubowsky, *Int. J. Solids Struct.* **2006**, *43*, 7727–7751.

[77] R. Díaz-Calleja, E. Riande, M. J. Sanchis, *Appl. Phys. Lett.* **2008**, *93*, 225–228.

[78] J. Leng, L. Liu, Y. Liu, K. Yu, S. Sun, *Appl. Phys. Lett.* **2009**, *94*, 211901.

[79] C. Keplinger, T. Li, R. Baumgartner, Z. Suo, S. Bauer, *Soft Matter* **2012**, *8*, 285–288.

[80] R. Kochetov, I. A. Tsekmes, P. H. F. Morshuis, *Smart Mater. Struct.* **2015**, *24*, 075019.

[81] E. G. Rochow, in *Silicon-Based Polym. Sci. - a Compr. Resour.* (Eds.: J.M. Zeigler, F.W.G. Fearon), American Chemical Society, **1990**, pp. xiii–xxii.

[82] M. Butts, J. Cella, C. D. Wood, G. Gillette, R. Kerboua, L. Leman, L. Lewis, S. Rubinsztajn, F. J. Schattenmann, J. Stein, et al., in *Kirk-Othmer Encycl. Chem. Technol.*, John Wiley & Sons, Inc., **2002**, pp. 1–89.

[83] J. E. Mark, in *Silicon-Based Polym. Sci. a Compr. Resour.* (Eds.: J.M. Zeigler, F.W.G. Fearon), American Chemical Society, **1990**, pp. 47–68.

[84] M. K. Jensen, A. Bach, O. Hassager, A. L. Skov, *Int. J. Adhes. Adhes.* **2009**, *29*, 687–693.

[85] J. de Jong, R. G. H. Lammertink, M. Wessling, *Lab Chip* **2006**, *6*, 1125–1139.

[86] F. de Buyl, *Int. J. Adhes. Adhes.* **2001**, *21*, 411–422.

[87] I. Flores-Vivian, V. Hejazi, M. I. Kozhukhova, M. Nosonovsky, K. Sobolev, *ACS Appl. Mater. Interfaces* **2013**, *5*, 13284–94.

[88] G. Sèbe, M. A. Brook, *Wood Sci. Technol.* **2001**, *35*, 269–282.

[89] Y. Xia, G. M. Whitesides, *Angew. Chemie Int. Ed.* **1998**, *37*, 550–575.

[90] M. A. Brook, H. U. Saier, J. Schnabel, K. Town, M. Maloney, *Ind. Eng. Chem. Res.* **2007**, *46*, 8796–8805.

[91] A. L. Larsen, P. Sommer-Larsen, O. Hassager, *e-Polymers* **2004**, *050*, 1–18.

[92] S. M. G. Frankær, M. K. Jensen, A. G. Bejenariu, A. L. Skov, *Rheol. Acta* **2012**, *51*, 559–567.

[93] J. E. Mark, in *Phys. Prop. Polym.* (Eds.: J. Mark, K. Ngai, W. Graessley, L. Mandelkern, E. Samulski, J. Koenig, G. Wignall), Cambridge University Press, Cambridge, United Kingdom, **2003**, pp. 3–71.

[94] P. Dvornic, in *Silicon-Containing Polym. - Sci. Technol. Their Synth. Appl.* (Eds.: R.G. Jones, W. Ando, J. Chojnowski), Springer - Verlag, Dordrecht, The Netherlands, **2000**, pp. 185–212.

[95] E. Delebecq, F. Ganachaud, *ACS Appl. Mater. Interfaces* **2012**, *4*, 3340–3352.

[96] E. Delebecq, N. Hermeline, A. Flers, F. Ganachaud, *ACS Appl. Mater. Interfaces* **2012**, *4*, 3353–3363.

[97] R. Kornbluh, R. Peirine, Q. Pei, S. Oh, J. Joseph, *Smart Struct. Mater. 2000 Electroact. Polym. Actuators Devices* **2000**, *3987*, 51–64.

[98] K. Meijer, M. Rosenthal, R. J. Full, *Struct. Mater.* **2001**, *4329*, 7–15.

[99] S. Michel, X. Q. Zhang, M. Wissler, C. Löwe, G. Kovacs, *Polym. Int.* **2009**, *59*, 391–399.

[100] X. Zhang, C. Löwe, M. Wissler, B. Jähne, G. Kovacs, *Adv. Eng. Mater.* **2005**, *7*, 361–367.

[101] F. Carpi, D. De Rossi, *ESA Interaction with Academia on Advanced Research Topics: ARIADNA: EAP-Based Artificial Muscles as an Alternative to Space Mechanisms by University of Pisa, University of Rome & Kayser Italia S.r.l.*, **2004**.

[102] F. Carpi, C. Salaris, D. De Rossi, *Smart Mater. Struct.* **2007**, *16*, S300–S305.

[103] F. Galantini, F. Carpi, G. Gallone, *Smart Mater. Struct.* **2013**, *22*, 104020.

[104] C. Jordi, A. Schmidt, G. Kovacs, S. Michel, P. Ermanni, *Smart Mater. Struct.* **2011**, *20*, 075003.

[105] U. Berardi, *J. Mech. Sci. Technol.* **2013**, *27*, 1–7.

[106] M. Y. Benslimane, H.-E. Kiil, M. J. Tryson, *Polym. Int.* **2010**, *59*, 415–421.

[107] T. Vu-Cong, C. Jean-Mistral, A. Sylvestre, *Smart Mater. Struct.* **2012**, *21*, 105036.

[108] M. Benslimane, H.-E. Kiil, M. J. Tryson, *Proc. SPIE* **2010**, *7642*, 764231–764231–11.

[109] M. Benslimane, P. Gravesen, P. Sommer-Larsen, *Proc. SPIE* **2002**, *4695*, 150–157.

[110] A. L. Skov, S. Vudayagiri, M. Benslimane, *Proc. SPIE* **2013**, *8687*, 86871I–86871I–8.

[111] A. L. Skov, A. Bejenariu, J. Bøgelund, M. Benslimane, A. D. Egede, *Proc. SPIE* **2012**, *8340*, 83400M–1–83400M–10.

[112] H. Stoyanov, P. Brochu, X. Niu, C. Lai, S. Yun, Q. Pei, *RSC Adv.* **2013**, *3*, 2272.

[113] S. Akbari, S. Rosset, H. R. Shea, **2013**, *8687*, 86871P–86871P–13.

[114] S. Michel, B. T. T. Chu, S. Grimm, F. A. Nüesch, A. Borgschulte, D. M. Opris, *J. Mater. Chem.* **2012**, *22*, 20736.

[115] K. Goswami, A. L. Skov, A. E. Daugaard, *Chem. - A Eur. J.* **2014**, *20*, 9230–3.

[116] G. B. Zhang, X. D. Fan, J. Kong, Y. Y. Liu, *Polym. Bull.* **2008**, *60*, 863–874.

[117] A. Chemtob, H. De Paz-Simon, C. Croutxé-Barghorn, S. Rigolet, *J. Appl. Polym. Sci.* **2014**, *131*, 39875.

[118] S. Schlögl, M. L. Trutschel, W. Chassé, I. Letofsky-Papst, R. Schaller, A. Holzner, G. Riess, W. Kern, K. Saalwächter, *Polymer* **2014**, *55*, 5584–5595.

[119] O. Van Den Berg, L. T. T. Nguyen, R. F. A. Teixeira, F. Goethals, C. Özdilek, S. Berghmans, F. E. Du Prez, *Macromolecules* **2014**, *47*, 1292–1300.

[120] M. A. Villar, M. A. Bibbo, E. M. Vallés, *Macromolecules* **1996**, *29*, 4072–4080.

[121] D. R. Paul, J. E. Mark, *Prog. Polym. Sci.* **2010**, *35*, 893–901.

[122] H. Zhao, Y.-J. Xia, Z.-M. Dang, J.-W. Zha, G.-H. Hu, *J. Appl. Polym. Sci.* **2013**, *127*, 4440–4445.

[123] S. Javadi, M. Razzaghi-Kashani, *Proc. SPIE* **2013**, *8687*, 86871K.

[124] H. Böse, D. Uhl, K. Flittner, H. Schlaak, *Proc. SPIE* **2011**, *7976*, 79762J–79762J–13.

[125] G. Kofod, H. Stoyanov, M. Kollosche, S. Risse, H. Ragusch, D. N. McCarthy, R. Waché, D. Rychkov, M. Dansachmüller, *Proc. SPIE* **2011**, *7976*, 79760J–1–12.

[126] G. Kofod, D. N. McCarthy, H. Stoyanov, M. Kollosche, S. Risse, H. Ragusch, D. Rychkov, M. Dansachmüller, R. Waché, *Proc. SPIE* **2010**, *7642*, 76420J–1–12.

[127] F. Carpi, D. De Rossi, *IEEE Trans. Dielectr. Electr. Insul.* **2005**, *12*, 835–843.

[128] T. Yamada, T. Ueda, T. Kitayama, *J. Appl. Phys.* **1982**, *53*, 4328–4332.

[129] D. A. G. Bruggeman, *Ann. Phys.* **1935**, 636–664.

[130] M. Razzaghi Kashani, S. Javadi, N. Gharavi, *Smart Mater. Struct.* **2010**, *19*, 035019.

[131] M. Razzaghi-Kashani, N. Gharavi, S. Javadi, *Smart Mater. Struct.* **2008**, *17*, 065035.

[132] N. Gharavi, M. Razzaghi-Kashani, N. Golshan-Ebrahimi, *Smart Mater. Struct.* **2010**, *19*, 025002.

[133] H. Zhao, L. Zhang, M. Yang, Z. Dang, J. Bai, **2015**, *092904*, 3–8.

[134] W. Wichiansee, A. Sirivat, *Mater. Sci. Eng. C* **2009**, *29*, 78–84.

[135] S. Thongbor, D. Pattavarakorn, *TIChE Int. Conf. 2011* **2011**, 1–5.

[136] M. Cazacu, M. Ignat, C. Racles, M. Cristea, V. Musteata, D. Ovezea, D. Lipcinski, *J. Compos. Mater.* **2014**, *48*, 1533–1545.

[137] E. Tuncer, S. M. Gubanski, *J. Phys. Condens. Matter* **2000**, *12*, 1873–1897.

[138] H. Zhao, D.-R. Wang, J.-W. Zha, J. Zhao, Z.-M. Dang, *J. Mater. Chem. A* **2013**, *1*, 3140–3145.

[139] H. Liu, L. Zhang, D. Yang, Y. Yu, L. Yao, M. Tian, *Soft Mater.* **2013**, *11*, 363–370.

[140] H. Stoyanov, P. Brochu, X. Niu, E. Della Gaspera, Q. Pei, *Appl. Phys. Lett.* **2012**, *100*, 262902.

[141] S. K. Yadav, I. J. Kim, H. J. Kim, J. Kim, S. M. Hong, C. M. Koo, *J. Mater. Chem. C* **2013**, *1*, 5463–5470.

[142] L. Z. Chen, C. H. Liu, C. H. Hu, S. S. Fan, *Appl. Phys. Lett.* **2008**, *92*, 263104.

[143] G. M. Ouyang, K. Y. Wang, X. Y. Chen, *2011 16th Int. Solid-State Sensors, Actuators Microsystems Conf. TRANSDUCERS'11* **2011**, 614–617.

[144] G. Ouyang, K. Wang, X. Y. Chen, *J. Micromechanics Microengineering* **2012**, *22*, 074002.

[145] L. J. Romasanta, P. Leret, L. Casaban, M. Hernández, M. A. de la Rubia, J. F. Fernández, J. M. Kenny, M. A. Lopez-Manchado, R. Verdejo, *J. Mater. Chem.* **2012**, *22*, 24705–24712.

[146] D. Yang, L. Zhang, H. Liu, Y. Dong, Y. Yu, M. Tian, *J. Appl. Polym. Sci.* **2012**, *125*, 2196–2201.

[147] S. Vudayagiri, S. Zakaria, L. Yu, S. S. Hassouneh, M. Benslimane, A. L. Skov, *Smart Mater. Struct.* **2014**, *23*, 105017.

[148] L. Yu, S. Vudayagiri, S. Zakaria, M. Y. Benslimane, A. L. Skov, *Proc. SPIE* **2014**, *9056*, 90560S.

[149] K. Goswami, A. E. Daugaard, A. L. Skov, *RSC Adv.* **2015**, *5*, 12792–12799.

[150] Z. Zhang, L. Liu, J. Fan, K. Yu, Y. Liu, L. Shi, J. Leng, *Proc. SPIE* **2008**, *6926*, 692610–1–692610–8.

[151] Y. Liu, L. Liu, Z. Zhang, J. Leng, *Smart Mater. Struct.* **2009**, *18*, 095024.

[152] B. Liu, M. T. Shaw, *J. Rheol.* **2001**, *45*, 641.

[153] P. Song, Z. J. Peng, Y. L. Yue, H. Zhang, Z. Zhang, Y. C. Fan, *Express Polym. Lett.* **2013**, *7*, 546–553.

[154] I. Babu, G. de With, *Compos. Sci. Technol.* **2014**, *91*, 91–97.

[155] S. K. Sharma, H. Gaur, M. Kulkarni, G. Patil, B. Bhattacharya, A. Sharma, *Compos. Sci. Technol.* **2013**, *77*, 42–51.

[156] E. Bortot, R. Springhetti, M. Gei, *J. Eur. Ceram. Soc.* **2014**, *34*, 2623–2632.

[157] M. Cazacu, C. Racles, M.-F. Zaltariov, A.-M. C. Dumitriu, M. Ignat, D. Ovezea, G. Stiubianu, *Smart Mater. Struct.* **2013**, *22*, 104008.

[158] X. Zhang, M. Wissler, B. Jaehne, R. Breonnimann, G. Kovacs, *Proc. SPIE* **2004**, *5385*, 78–86.

[159] D. M. Opris, D. Crespy, C. Löwe, M. Molberg, F. Nüesch, *Proc. SPIE* **2009**, *7287*, 72870L–72870L–8.

[160] M. Molberg, D. Crespy, P. Rupper, F. Nüesch, J.-A. E. Månson, C. Löwe, D. M. Opris, *Adv. Funct. Mater.* **2010**, *20*, 3280–3291.

[161] D. M. Opris, M. Molberg, C. Walder, Y. S. Ko, B. Fischer, F. A. Nüesch, *Adv. Funct. Mater.* **2011**, *21*, 3531–3539.

[162] D. Yang, M. Tian, W. Wang, D. Li, R. Li, H. Liu, L. Zhang, *Electrochim. Acta* **2013**, *87*, 9–17.

[163] J. E. Q. Quinsaat, M. Alexandru, F. A. Nueesch, H. Hofmann, A. Borgschulte, D. M. Opris, *J. Mater. Chem. A* **2015**, *3*, 14675–14685.

[164] J. E. Q. Quinsaat, F. A. Nüesch, H. Hofmann, D. M. Opris, *RSC Adv.* **2013**, *3*, 6964–6971.

[165] P. Mazurek, S. Hvilsted, A. L. Skov, *Proc. SPIE* **2014**, *9056*, 90562T.

[166] P. Mazurek, A. E. Daugaard, M. Skolimowski, S. Hvilsted, A. L. Skov, *RSC Adv.* **2015**, *5*, 15379–15386.

[167] F. Carpi, G. Gallone, F. Galantini, D. De Rossi, *Adv. Funct. Mater.* **2008**, *18*, 235–241.

[168] F. Carpi, G. Gallone, F. Galantini, D. De Rossi, *Proc. SPIE* **2008**, *6927*, 692707–692707–11.

[169] G. Gallone, F. Galantini, F. Carpi, *Polym. Int.* **2010**, *59*, 400–406.

[170] H. Liu, L. Zhang, D. Yang, N. Ning, Y. Yu, L. Yao, B. Yan, M. Tian, *J. Phys. D. Appl. Phys.* **2012**, *45*, 485303.

[171] A. H. A. Razak, P. Szabo, A. L. Skov, *RSC Adv.* **2015**, *5*, 53054–53062.

[172] S. Risse, B. Kussmaul, H. Krüger, G. Kofod, *Adv. Funct. Mater.* **2012**, *22*, 3958–3962.

[173] H. Böse, D. Uhl, R. Rabindranath, *Proc. SPIE* **2012**, *8340*, 83402E.

[174] F. B. Madsen, L. Yu, S. Hvilsted, A. L. Skov, *Proc. SPIE* **2015**, *9430*, 94301D–1–94301D–14.

[175] F. B. Madsen, L. Yu, P. S. Mazurek, A. L. Skov, *Unpublished* **2015**.

[176] B. Kussmaul, S. Risse, G. Kofod, R. Waché, M. Wegener, D. N. McCarthy, H. Krüger, R. Gerhard, *Adv. Funct. Mater.* **2011**, *21*, 4589–4594.

[177] B. Kussmaul, S. Risse, M. Wegener, G. Kofod, H. Krüger, *Smart Mater. Struct.* **2012**, *21*, 064005.

[178] S. Risse, B. Kussmaul, H. Krüger, G. Kofod, *RSC Adv.* **2012**, *2*, 9029–9035.

[179] C. Racles, M. Cazacu, B. Fischer, D. M. Opris, *Smart Mater. Struct.* **2013**, *22*, 104004.

[180] C. Racles, M. Alexandru, A. Bele, V. E. Musteata, M. Cazacu, D. M. Opris, *RSC Adv.* **2014**, *4*, 37620.

[181] C. Racles, a. Bele, M. Dascalu, V. E. Musteata, C. D. Varganici, D. Ionita, S. Vlad, M. Cazacu, S. J. Dünki, D. M. Opris, *RSC Adv.* **2015**, *5*, 58428–58438.

[182] F. B. Madsen, I. Dimitrov, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Polym. Chem.* **2013**, *4*, 1700–1707.

[183] F. B. Madsen, A. E. Daugaard, S. Hvilsted, M. Y. Benslimane, A. L. Skov, *Smart Mater. Struct.* **2013**, *22*, 104002.

[184] F. B. Madsen, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Proc. SPIE* **2013**, *8687*, 86871H.

[185] F. B. Madsen, I. Javakhishvili, R. E. Jensen, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Polym. Chem.* **2014**, *5*, 7054–7061.

[186] F. B. Madsen, L. Yu, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Proc. SPIE* **2015**, *9430*, 943012–1–943012–12.

[187] A. Bele, M. Cazacu, C. Racles, G. Stiubianu, D. Ovezea, M. Ignat, *Adv. Eng. Mater.* **2015**, *17*, 1302–1312.

[188] S. J. Dünki, Y. S. Ko, F. A. Nüesch, D. M. Opris, *Adv. Funct. Mater.* **2015**, *25*, 2467–2475.

[189] S. J. Dünki, M. Tress, F. Kremer, S. Y. Ko, F. A. Nüesch, C.-D. Varganici, C. Racles, D. M. Opris, *RSC Adv.* **2015**, *5*, 50054–50062.

[190] L. Zhang, D. Wang, P. Hu, J.-W. Zha, F. You, S.-T. Li, Z.-M. Dang, *J. Mater. Chem. C* **2015**, *3*, 4883–4889.

[191] F. B. Madsen, L. Yu, A. E. Daugaard, S. Hvilsted, A. L. Skov, *RSC Adv.* **2015**, *5*, 10254–10259.

[192] L. H. Sperling, *Mater. Sci.* **1994**, 3–38.

[193] L. H. Sperling, *Polym. Adv. Technol.* **1996**, *7*, 197–208.

[194] S. M. Ha, W. Yuan, Q. Pei, R. Pelrine, S. Stanford, *Adv. Mater.* **2006**, *18*, 887–891.

[195] S. M. Ha, W. Yuan, Q. Pei, R. Pelrine, S. Stanford, *Smart Mater. Struct.* **2007**, *16*, S280–S287.

[196] S. M. Ha, I. S. Park, M. Wissler, R. Pelrine, S. Stanford, K. J. Kim, G. Kovacs, Q. Pei, *Proc. SPIE* **2008**, *6927*, 69272C–69272C–9.

[197] G. Mathew, J. Rhee, C. Nah, D. Leo, *Polym. Eng. Sci.* **2006**, *46*, 1455–1460.

[198] C. Tugui, G. T. Stiubianu, M. Iacob, C. Ursu, A. Bele, S. Vlad, M. Cazacu, *J. Mater. Chem. C* **2015**, *3*, 8963–8969.

[199] L. González, A. L. Skov, S. Hvilsted, *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51*, 1359–1371.

[200] L. González, L. Yu, S. Hvilsted, A. L. Skov, *RSC Adv.* **2014**, *4*, 36117–36124.

[201] L. Yu, F. B. Madsen, S. Hvilsted, A. L. Skov, *Proc. SPIE* **2015**, *9430*, 94300T–1–94300T–11.

[202] L. Yu, F. B. Madsen, S. Hvilsted, A. L. Skov, *RSC Adv.* **2015**, *5*, 49739–49747.

[203] J. E. Mark, *Br. Polym. J.* **1985**, *17*, 144–148.

[204] G. D. Genesky, B. M. Aguilera-Mercado, D. M. Bhawe, F. A. Escobedo, C. Cohen, *Macromolecules* **2008**, *41*, 8231–8241.

[205] T. L. Smith, B. Haidar, J. L. Hedrick, *Rubber Chem. Technol.* **1990**, *63*, 256–264.

[206] G. B. Shah, R. W. Winter, *Macromol. Chem. Phys.* **1996**, *197*, 2201–2208.

[207] J. E. Mark, *Prog. Polym. Sci.* **2003**, *28*, 1205–1221.

[208] Z.-M. Zhangt, J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.* **1982**, *20*, 473–480.

[209] P. Xu, J. E. Mark, *Polymer* **1992**, *33*, 1843–1848.

[210] M. A. Llorente, A. L. Andrady, J. E. Mark, *J. Polym. Sci. Polym. Phys. Ed.* **1981**, *19*, 621–630.

[211] M. Y. Tang, J. E. Mark, *Macromolecules* **1984**, *17*, 2616–2619.

[212] B. Viers, J. Mark, *J. Macromol. Sci. Part A Pure Appl. Chem.* **2007**, *44*, 131–138.

[213] J. E. Mark, A. L. Andrady, *Rubber Chem. Technol.* **1981**, *54*, 366–373.

[214] S.-J. Pan, J. E. Mark, *Polym. Bull.* **1982**, *7*, 553–559.

[215] A. G. Bejenariu, L. Yu, A. L. Skov, *Soft Matter* **2012**, *8*, 3917–3923.

[216] A. G. Bejenariu, M. Boll, M. R. Lotz, C. Vraa, A. L. Skov, *Proc. SPIE* **2011**, *7976*, 79762V–79762V–8.

[217] F. B. Madsen, A. E. Daugaard, C. Fleury, S. Hvilsted, A. L. Skov, *RSC Adv.* **2014**, *4*, 6939–6945.

[218] F. Chambon, H. H. Winter, *J. Rheol.* **1987**, *31*, 683.

[219] J. Goff, S. Sulaiman, B. Arkles, in *ACS Bost. 2015*, **2015**.

[220] L.-H. Cai, T. E. Kodger, R. E. Guerra, A. F. Pegoraro, M. Rubinstein, D. A. Weitz, *Adv. Mater.* **2015**, *27*, 5132–5240.

[221] F. Carpi, I. Anderson, S. Bauer, G. Frediani, G. Gallone, M. Gei, C. Graaf, C. Jean-Mistral, W. Kaal, G. Kofod, et al., *Smart Mater. Struct.* **2015**, *24*, 105025.

[222] W. Yuan, H. Li, P. Brochu, X. Niu, Q. Pei, *Int. J. Smart Nano Mater.* **2010**, *1*, 40–52.

[223] "http://softroboticstoolkit.com/," **2015**.

[224] "http://cdoomany.tumblr.com/," **2015**.

[225] S. Javadi, M. Razzaghi-Kashani, *Proc. SPIE* **2010**, *7642*, 76421E–76421E–12.

[226] D. Khastgir, K. Adachi, *J. Polym. Sci. Part B Polym. Phys.* **1999**, *37*, 3065–3070.

[227] J. P. Szabo, J. A. Hiltz, C. G. Cameron, R. S. Underhill, J. Massey, B. White, J. Leidner, *Proc. SPIE* **2003**, *5051*, 180–190.

[228] P. Lotz, M. Matysek, P. Lechner, M. Hamann, H. F. Schlaak, *Proc. SPIE* **2008**, *7976*, 692723–692723–10.

[229] A. Bele, M. Cazacu, G. Stiubianu, S. Vlad, M. Ignat, *Compos. Part B Eng.* **2015**, *68*, 237–245.

[230] A. Bele, G. Stiubianu, C.-D. Varganici, M. Ignat, M. Cazacu, *J. Mater. Sci.* **2015**, *50*, 6822–6832.

[231] G. L. Wang, Y. Y. Zhang, L. Duan, K. H. Ding, Z. F. Wang, M. Zhang, *J. Appl. Polym. Sci.* **2015**, *132*, 42613.

[232] G. Gallone, F. Carpi, D. De Rossi, G. Levita, A. Marchetti, *Mater. Sci. Eng. C* **2007**, *27*, 110–116.

[233] N. Gharavi, M. Razzaghi Kashani, A. Moradi, *Proc. SPIE* **2010**, *7642*, 764233–1–764233–7.

[234] Z. Jia, S. Chen, J. Zhang, *J. Macromol. Sci. Part B* **2012**, *51*, 2449–2461.

[235] Z. M. Dang, B. Xia, S. H. Yao, M. J. Jiang, H. T. Song, L. Q. Zhang, D. Xie, *Appl. Phys. Lett.* **2009**, *94*, 042902.

[236] M. Tian, Z. Wei, X. Zan, L. Zhang, J. Zhang, Q. Ma, N. Ning, T. Nishi, *Compos. Sci. Technol.* **2014**, *99*, 37–44.

[237] S. S. Hassouneh, A. E. Daugaard, A. L. Skov, *Macromol. Mater. Eng.* **2015**, *300*, 542–550.

[238] L. J. Romasanta, M. Hernández, M. A. López-Manchado, R. Verdejo, *Nanoscale Res. Lett.* **2011**, *6*, 508.

[239] F. B. Madsen, L. Yu, A. E. Daugaard, S. Hvilsted, A. L. Skov, *Polymer* **2014**, *55*, 6212–6219.

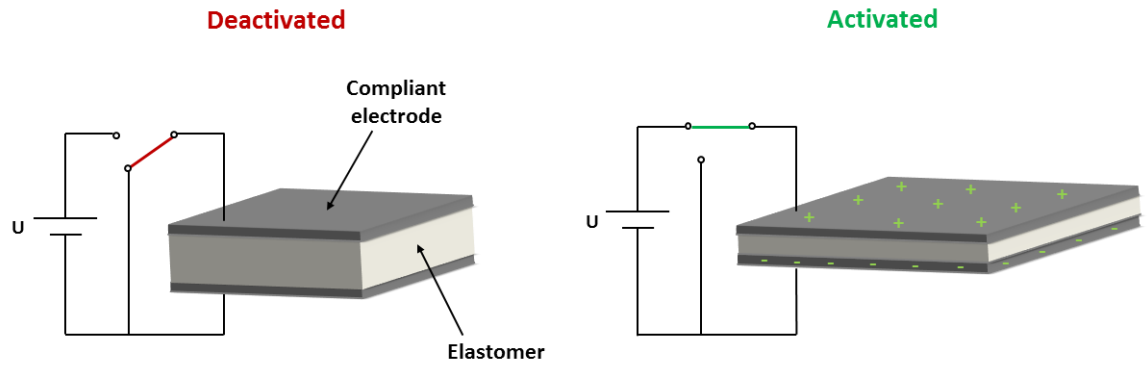



*Figure 1.* Schematic illustration of the transduction principle of DET.

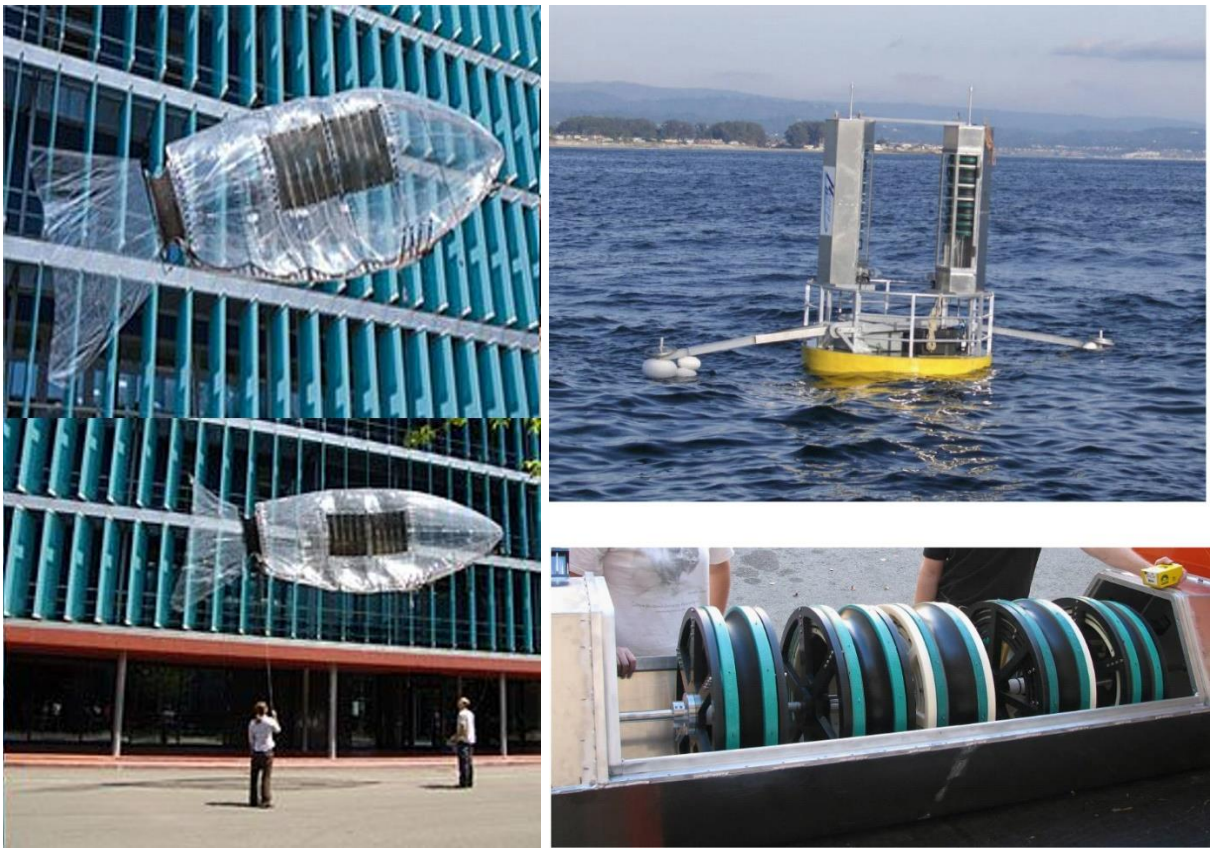


*Figure 2.* Examples of extraordinary DET applications. Left: Flying fish blimp by EMPA.[40] Right: Dielectric elastomer ocean wave power generator by SRI International.[41]

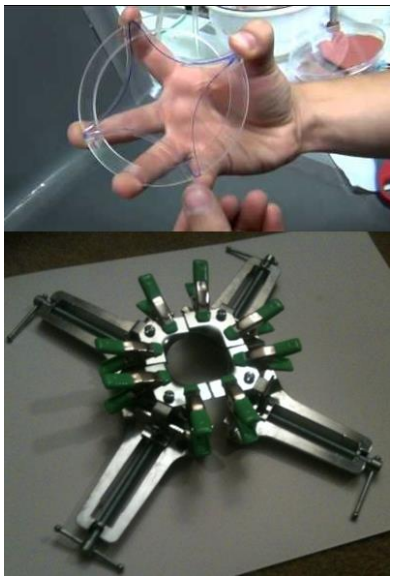


*Figure 3*. Pre-straining devices. The top picture illustrates a simple frame which is applicable when the dielectric elastomer is adhesive.[223] The bottom picture illustrates a mechanical solution to homogeneous stretching.[224]

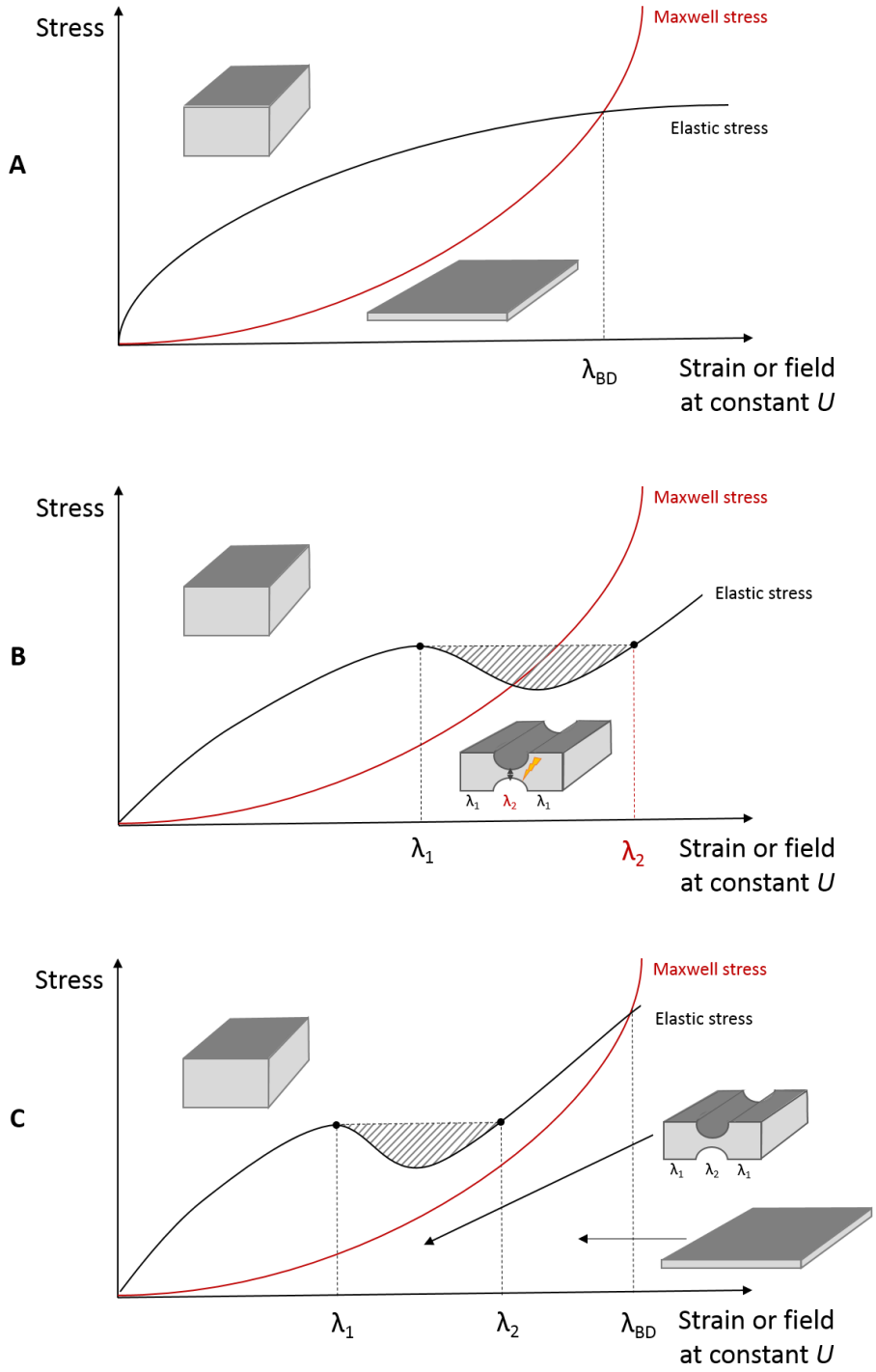



*Figure 4.* Illustration of stress-strain diagrams of elastomers with various behaviours with respect to electromechanical instability (EMI). A) Elastomer with no EMI. Ideally, the elastomer fails at the strain that corresponds to the intrinsic breakdown strength of the elastomer. B) Elastomer with snap-through and EMI. The elastomer will break down at $\lambda=\lambda_1$ as the snap-through faciliates dielectric breakdown as the Maxwell stress exceeds the elastic stress before reaching $\lambda=\lambda_2$. C) Elastomer with snap-through but no EMI due to pre-straining. The snap-through will proceed without breakdown and will, as for the elastomer in A), ideally break down at the intrinsic breakdown strength of the elastomer.

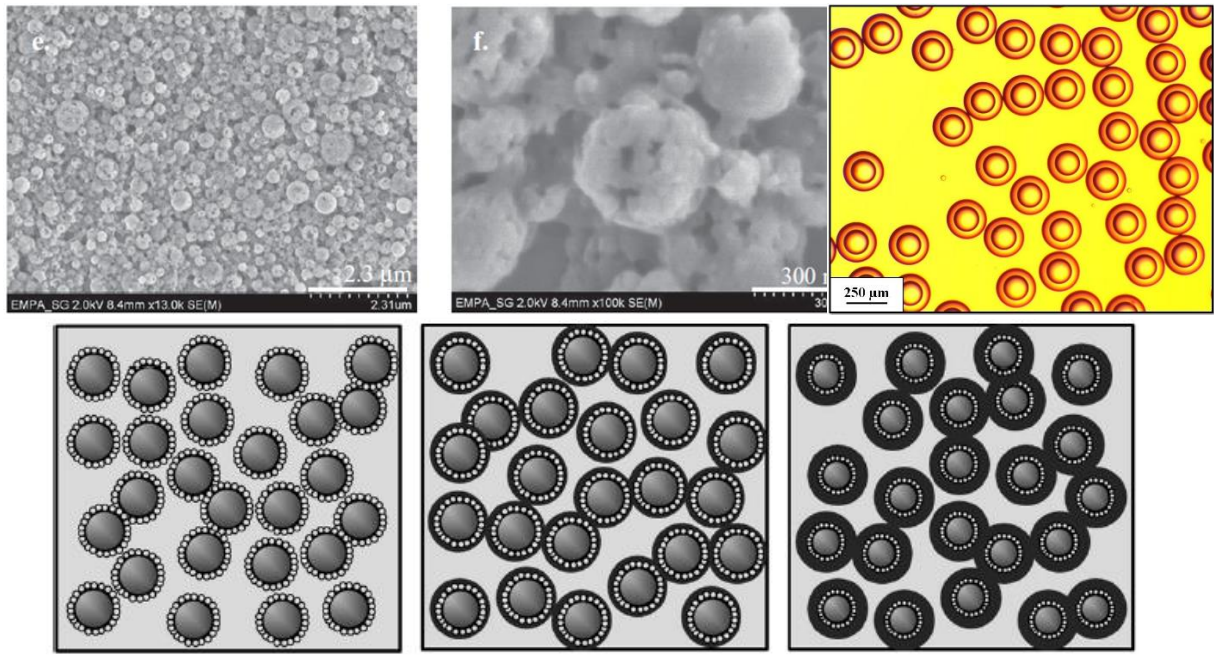



*Figure 5.* Examples of core-shell or encapsulated fillers for DET applications. Top left and middle: Encapsulated PANI (SEM micrographs).[160] Top right: Liquid core-shell particles for liquid high permittivity fillers (microscopy)[166] Reproduced with permission.[166] 2015, The Royal Society of Chemistry. Bottom: Dopamine-covered Ag/SiO2 core-shell particles. Reproduced with permission.[162] 2015, Elsevier.

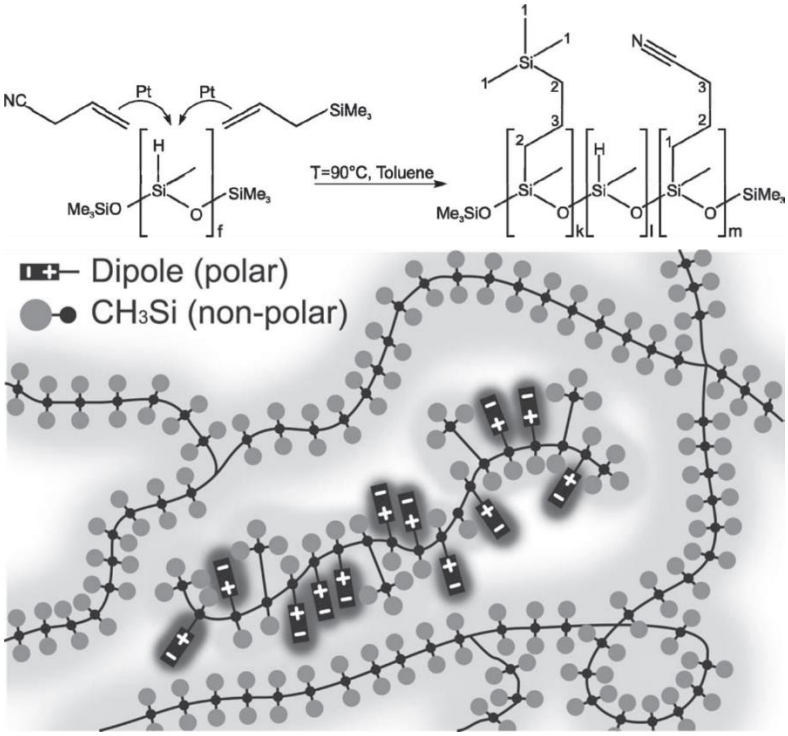



*Figure 6.* Cyano-functionalised siloxane acting both as a high permittivity filler and a plasticiser in the silicone matrix.[172]

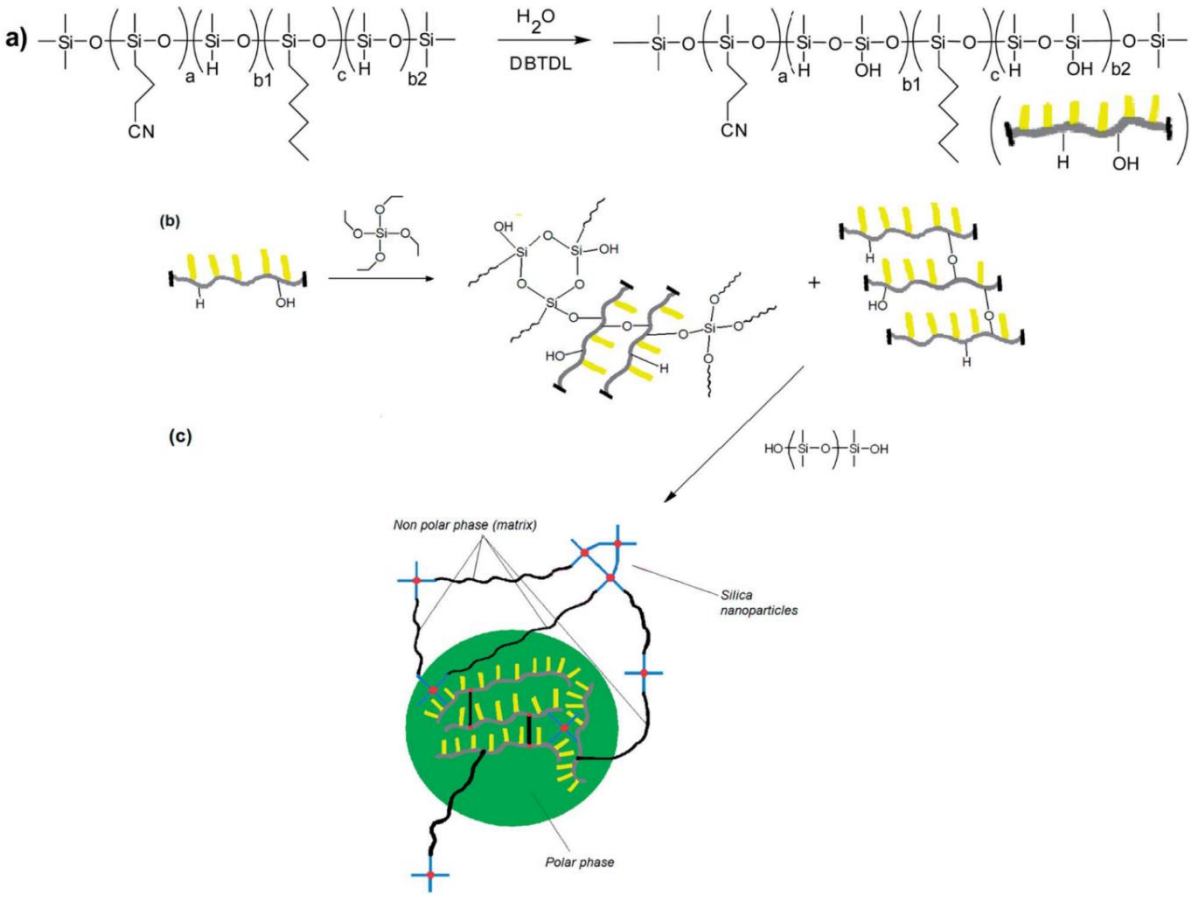



*Figure 7.* Schematic illustration of the route to improved cyanopropyl-functional PDMS networks. Reproduced with permission.[181] 2015, The Royal Society of Chemistry.

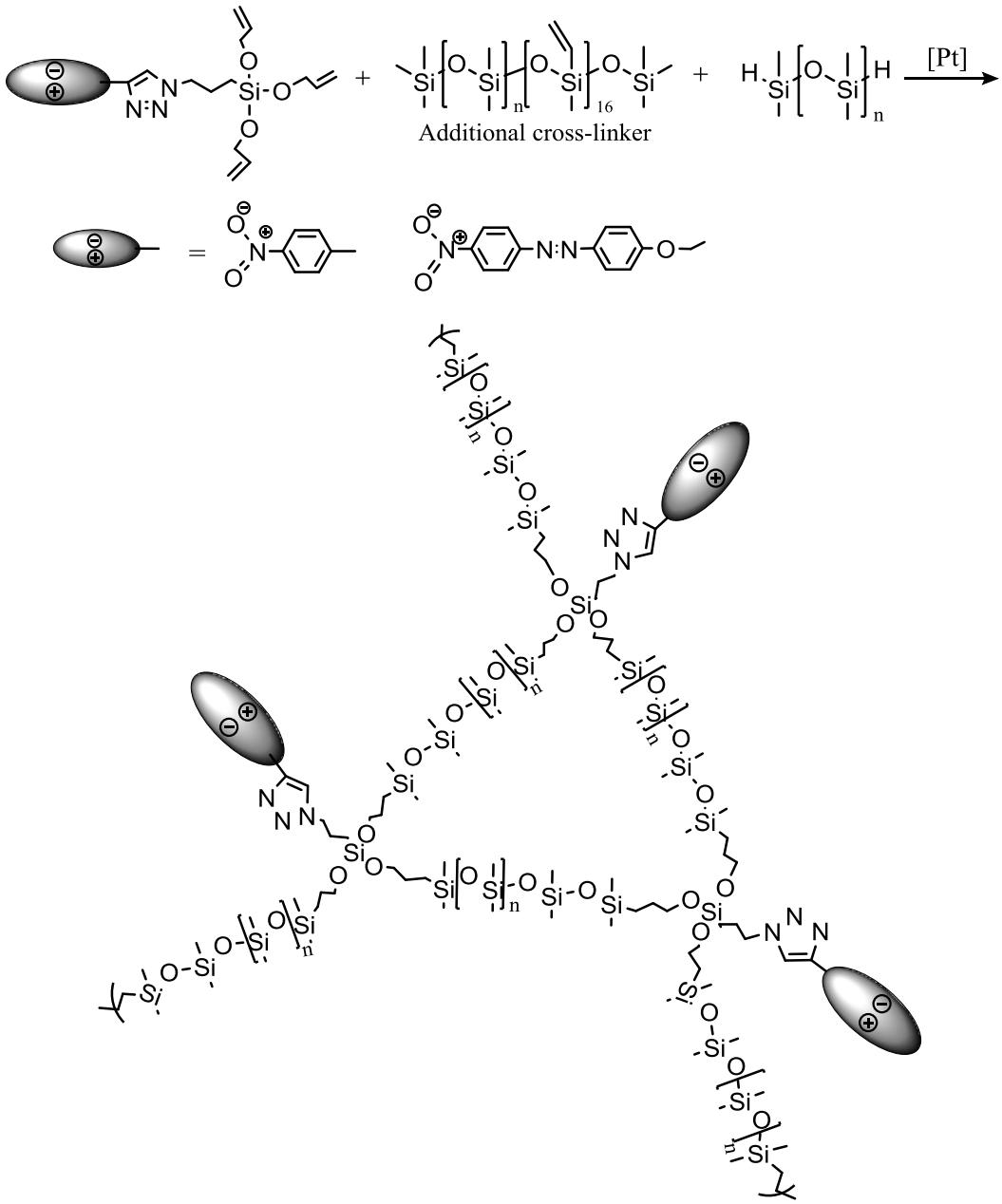



*Figure 8.* Cross-linking reaction between nitrobenzene and azonitrobenzene-functional cross-linkers and PDMS. Reproduced with permission.[183] 2013, IOPscience.

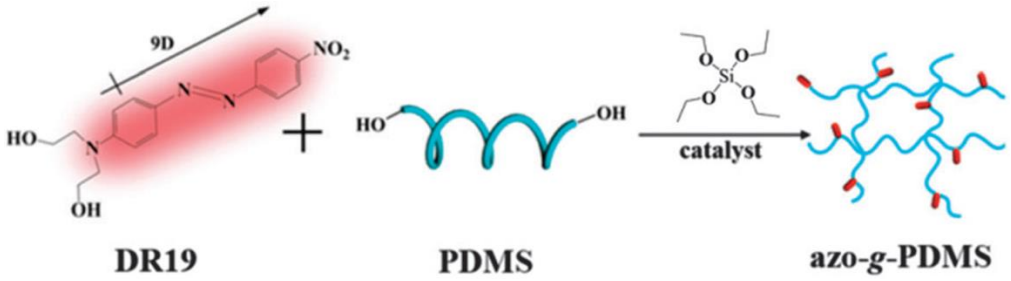



*Figure 9.* The synthetic approach to the nitroazobenzene-grafted PDMS network using a condensation cure reaction. Reproduced with permission.[190] 2015, The Royal Society of Chemistry.

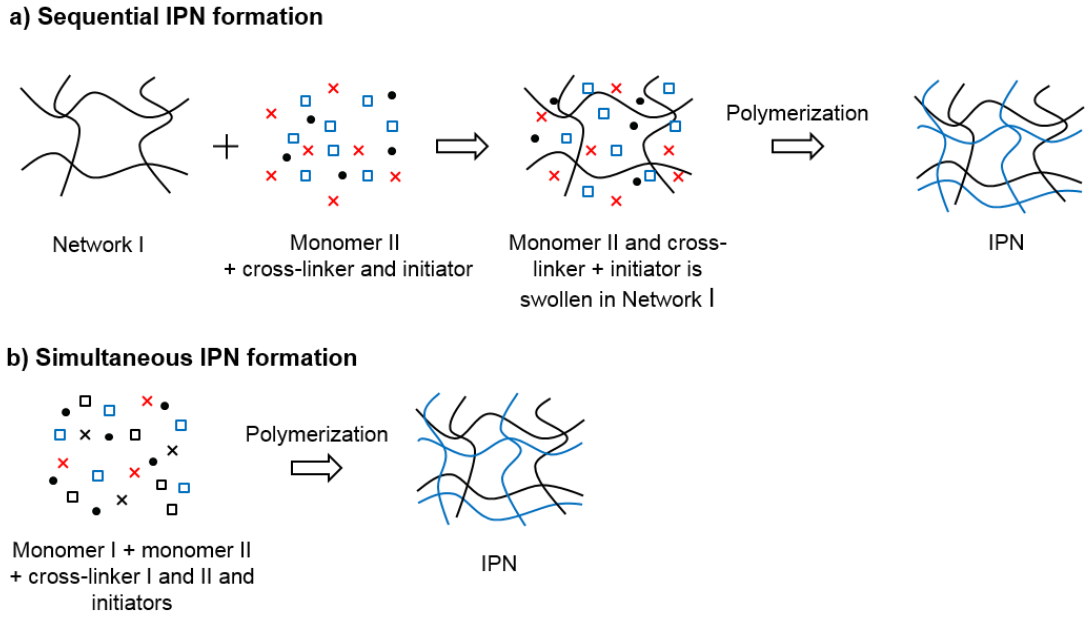



*Figure 10.* Schematic illustration of sequential (a) and simultaneous (b) IPN formation.

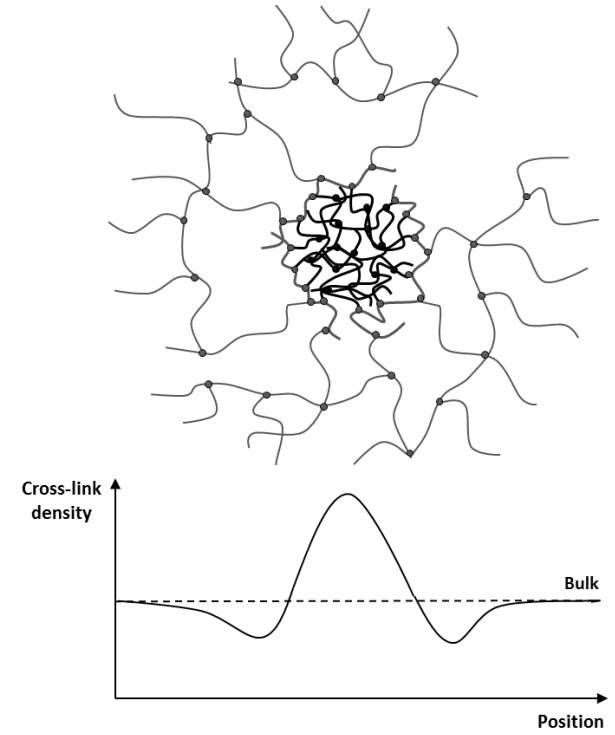



*Figure 11.* Schematic illustration of efficient cross-linking density in a heterogeneous bimodal network. Reproduced with permission.[217] 2014, The Royal Society of Chemistry.

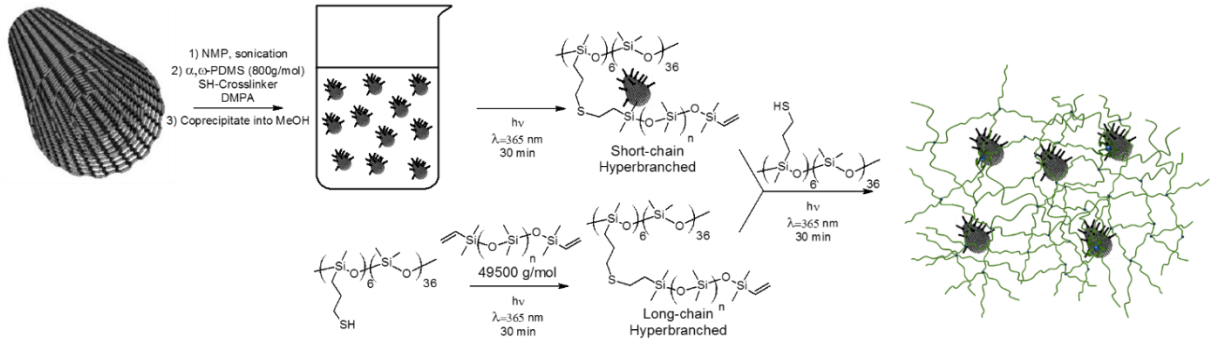
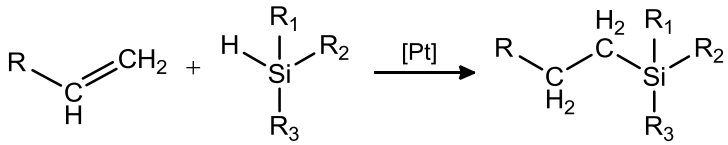
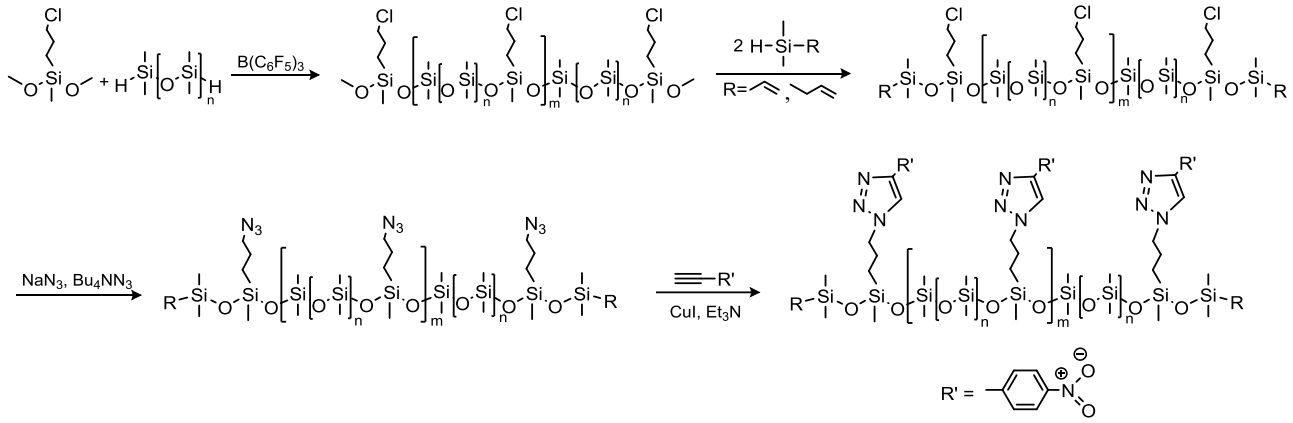



*Figure 12.* Preparation procedure for MWCNT-filled, thiolene-cured heterogeneous bimodal silicone networks. Reproduced with permission.[149] 2015, The Royal Society of Chemistry.




*Scheme 1.* Hydrosilylation reaction, where R, $R_1$, $R_2$ and $R_3$ can be various groups such as $CH_3$, phenyl-groups or polymer chains.




*Scheme 2.* Synthetic route to azido- and CuAAC-functionalised copolymers. Reproduced with permission.[185] 2014, The Royal Society of Chemistry.

*Table 1*. Properties of commercial silicone elastomers for DETs.

| **Base elastomer** | **$\varepsilon$'@0.1 Hz** | **$\varepsilon$'@1 MHz** | **tan δ @0.1 Hz** | ***Y*** **[MPa]** | **Maximum strain [%]** | **Thickness of film for $E_B$ [μm]** | **$E_B$ [V/μm]** | **Maximum thickness actuation strain [%]** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|
| BJB TC5005 with Plasticiser (40 phr stated) | 5.2[a)] | 4.2 | 0.7/5.2[a)] | 0.050 | 300 | 1000 pre-strained to ~500 | 10[b)] | 11 @ 10V/μm | [103] |
| Silastic LC-20-2004 with self-clearing electrodes | n.a. | n.a. | n.a. | n.a. | 700[c)] | 100 pre-strained to ~25 | 250 (pre-strained) | 50 @ 230V/μm | [222] |
| Neukasil RTV-23 | 2.5 | 2.5 | n.a. | 0.4 (when pre-strained 50%) | n.a. | n.a. | n.a. | 1 in cyclic experiment | [52] |
| HS3 Dow Corning (centrifuged)[d)] | 2.8 | 2.8 | 0.005[e)] | 0.1 | 2.8 | 225 pre-strained to ~80 | 110 (pre-strained 68% in both directions) | 48 @ 110 V/ μm | [62] |
| Nusil CF19-2186 | 2.8 | 2.8 | 0.005[e)] | 1.0[c)] | 600[c)] | 50 pre-strained to ~24 | 350 (pre-strained 45% in both directions) | 39[f)] | [3,62] |
| Sylgard 186 | n.a. | n.a. | n.a. | n.a. | n.a. | 31 pre-strained to ~6 | na | 70 @ 3.7 kV | [113] |
| Sylgard 186 | 2.8 | n.a. | n.a. | 0.7 | n.a. | n.a. | 144[b)] | 32 @ 144 V/ μm | [2] |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fluorosilicone Dow Corning 730 (centrifuged to remove particles) | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | 80[b)] | 28 @ 80 V/ μm | [2] |
| Danfoss PolyPower film | 2.6 (pre-strained) | n.a. | n.a. | n.a. | n.a. | 100 pre-strained to 71 | 50 | 7 @ 3kV | [104] |
| Silastic LC-50-2004 | 2.8 | n.a. | n.a. | 0.9 | n.a. | 60-100 | 105 | n.a. | [110,111] |
| LR 3005/50 | 3.0 | n.a. | n.a. | 0.8 | n.a. | 60-100 | 115 | n.a. | [110,111] |
| LR3043/30 | 2.8 | n.a. | n.a. | 0.8 | n.a. | 60-100 | 118 | n.a. | [110,111] |
| LR3043/50 | 2.8 | n.a. | n.a. | 1.5 | n.a. | 60-100 | 130 | n.a. | [110,111] |
| Wacker Silpuran 6000/10 | n.a. | n.a. | n.a. | 0.22 – 0.32 | n.a. | 10,000 pre-strained to 2,000 | 120 (pre-strained) | n.a. | [112] |

[a)] @1 Hz; [b)] The breakdown strength is determined from the actuation plot; [c)] Data from data sheet supplied by supplier; [d)] Elastomer no longer available from Dow Corning; [e)] @1 kHz; [f)] Field not available.

*Table 2.* $TiO_2$-filled PDMS elastomers.

| **Base elastomer** | **Filler/plasticiser** | **Method of dispersion** | **Content** | ***ε'*** | **tan δ @0.1 Hz** | ***Y*** **[MPa]** | **Maximum strain [%]** | **Thickness of film for $E_B$ [µm]** | ***$E_B$*** **[V/µm]** | **Maximum actuation strain [%]** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sineskin A/B/C 50% silicone) | $TiO_2$ (Rutile, 10 µm) + plasticizer (C) | Mech. mix. | 30 wt % | 7.5 @10 Hz | 0.08 | 0.016 | 400 | 1000 | 10[d)] | 11 @10 V/µm | [127] |
| HO-PDMS-OH , condens. cure | $TiO_2$ (50 nm), 100 phr PDMS oil | US + THF, magn. mix. | 30 phr | 3.5 @5 kHz | n.a. | 0.1 | n.a. | 100 | 35[d)] | 17 @35 V/µm[a] | [138] |
| v-PDMS, addition cure | $TiO_2$ (25 nm), PEG-PDMS | Ball milling | 5 wt% | 3.9 @100 Hz | n.a. | 0.57 | n.a. | n.a. | n.a. | [b)] | [143,144] |
| Silastic 3481 | $TiO_2$ (Rutile, 3 µm) | US + THF, solvent casting | 30 phr | 6 @10 Hz | 0.06 @10 Hz | 0.669 | 6 | n.a. | n.a. | 18 @50 V/µm[c)] | [139] |
| PDMS w. 28 phr $SiO_2$, condens. cure | $TiO_2$ and $SiO_2$ | Yanke-Kunkel lab.mix. | 50 phr $TiO_2$ | 5 @1 Hz | 0.02 @1Hz | 1.02 | 635 | n.a. | n.a. | 0.5 @0.51 V/µm | [136] |
| Sylgard 184 | $TiO_2$ (200 nm) | Mech. mix, electrical | 11 vol %[d)] | 5.5 @1 kHz | 0.006 @1 kHz | 2.2[e)] | 150 | n.a. | n.a. | n.a. | [130,225] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | field orient. | | | | | | | | | |
| Silpuran 6000/10 | $TiO_2$ (Rutile, 20 nm) functionalized with short PDMS chains | Mixed in isopar, US | 5 wt% | 20% inc. comp. to PDMS [f] | n.a. | 1.5 | n.a. | n.a. | 80[g] | 30 @80 V/µm | [140] |
| Powersil XLR630 | $TiO_2$ T805 Evonik (21 nm) HMDS treated | Speedmix. | 9 wt% | 3.32 @0.1 Hz | 0.008 @1 kHz | 0.549 | n.a. | 30-90 | 107 | n.a. | [147,148] |
| LR 3005/50 | $TiO_2$ T805 Evonik (21 nm), HMDS treated | Speedmix. | 9 wt% | 3.18 @0.1 Hz | n.a. | 0.224 | n.a. | 30-90 | 136 | n.a. | [147] |

[a] Areal strain
[b] Reduced driving voltage from 250V to 230 V and reduced response time from 9 µs to 6 µs
[c] @ 5 % pre-strain
[d] Dielectrophoretically oriented sample
[e] @ 50% strain
[f] Calculated from the blocking force.
[g] From the actuation plot

*Table 3.* Various titanate-filled PDMS systems.

| **Base elastomer** | **Filler/plasticizer** | **Method of dispersion** | **Content** | ***ε'*** | **tan δ** | ***Y*** **[MPa]** | **Max. strain [%]** | **Thickness of film for $E_B$ [µm]** | **$E_B$ [V/µm]** | **Maximum actuation strain [%]** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PDMS | $BaTiO_3$ (100nm) + 100 phr silicone oil | Mech. mix. | 100 phr $BaTiO_3$ | 5 @1 kHz-1 MHz | n.a. | 0.15 | n.a. | n.a. | n.a. | 13.5 @35 V/µm[a)] | [133] |
| Shinetsu KE103 | $BaTiO_3$ (100-500 nm) | Electrical field orient. | 44 wt% | 5.8 @1 kHz | 0.03 | 0.312 | n.a. | n.a. | n.a. | [b)] | [226] |
| Elastosil 601 | $BaTiO_3$ | Pebble mill w. toluene | 30 wt% | 4 @1Hz | n.a. | 2.0 | n.a. | 150 | 25 | 0.4 @25 V/µm | [227] |
| TC5005–A/B-C | $BaTiO_3$, 35% plasticizer | Mech. blender | 10 wt% $BaTiO_3$ | 300[c)] | 0.0008 | n.a. | 140 | 50 | 103 | 28 @8.5 V/µm | [150] |
| TC5005–A/B-C | $BaTiO_3$, 30% plasticiser | High velocity agitator | 10 wt% $BaTiO_3$ | 8[c)] | 0.016 | n.a. | 250 | n.a. | n.a. | n.a. | [151] |
| RT625 | $BaTiO_3$,(<3 µm) | High speed mixer | 20 vol% | 7.5 @1 kHz | 0.0067 | 0.2 | 450 | 250 | 40 | 8 @22 V/µm | [124] |
| Elastosil P7670 | $BaTiO_3$ (50-70 nm) | Sonication, mech. mix | 1.6 vol% | 4.2[c)] | n.a. | 0.125 | n.a. | 4-100 | 27 | n.a. | [228] |
| v-PDMS, peroxide cure | $BaTiO_3$ (<3 µm), 5 phr Pluoronic L-31 | Mech. mix., $CHCl_3$ | 5 wt% | 4.17 @10 Hz | 0.11 | 0.27 | n.a. | 500-1000 | 13 | n.a. | [229] |
| v-PDMS w. 10 wt% $SiO_2$, peroxide cure | $BaTiO_3$ hydrophob. (<3 µm) | Yanke-Kunkel laboratory mixer | 5 wt% $BaTiO_3$ | 3.67 @10 Hz | 0.0027 | 0.81 | 5.4 | n.a. | n.a. | [e)] | [230] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Rhodorsil MF620U | CCTO (5 µm) | Roll milling | 20 wt% | 5.3 @0.1 Hz | 0.05 | n.a. | n.a. | n.a. | n.a. | 6.0 @25 V/µm | [145] |
| LR3005/50 | CCTO | Speedmixing | 6 wt% | 4.09 @1 MHz | 0.002 | 0.183 | n.a. | 30-90 | 123 | n.a. | [147] |
| RTV3483 | CCTO (300 nm) | THF, US | 2 wt% | 4.37 @50 Hz | 0.013 | 0.29 | n.a. | 500 | 10[f)] | 14.3 @10 V/µm | [231] |
| TC5005 A/B-C 45% C, silicone) | PMN-PT | Mech. mix. | 10 vol% | 10.2 @1 kHz | 0.08 | 0.1 | 575 | n.a. | n.a. | n.a. | [232] |
| PDMS, peroxide cure | PMN (1.5 µm). Silicone oil | Two roll mill | 20 vol% | 5.2 @1 kHz | n.a. | 1.0 | n.a. | n.a. | 53[f)] | 7.9 @53 V/µm | [146] |
| APH-20, peroxide cure | Vinylsilane-PZT (<500 nm) | Brabender mixer and two roll mill | 10 wt% | 3.7 @1 kHz | 0.08 | 2.21[g] | n.a. | n.a. | n.a. | Increased actuation strain was observed | [233] |
| v-PDMS | PZT | Speedmix. | 40 vol% | 28 | 0.022 | 4.8 | 30 | n.a. | n.a. | n.a. | [154] |

[a)] Areal strain, 350% increased actuation strain; [b)] Piezoelectric response increased with loading; [c)] Frequency not reported; [d)] 100% improved actuation strain at 20 V/µm; [e)] Energy harvesting potential was evaluated, showing 157 V/mm in output voltage for the given sample; [f)] From the actuation plot; [g)] Taken at 25% strain

*Table 4.* Clays used as fillers in DET applications.

| **Base elastomer** | **Filler** | **Method of dispersion** | **Content** | ***ε'*** | **tan δ @0.1 Hz** | ***Y*** **[MPa]** | **Max. strain [%]** | **Ref** |
|---|---|---|---|---|---|---|---|---|
| APH-20 peroxide cure | MMT cloisite 15A | High shear mix. brabender and roll mill | 5 wt% | 3.7 @1 kHz | 0.07 | 0.347[c)] | 854 | [131] |
| Silastic 3481 | MMT cloisite 15A | Low shear solvent mixing | 5 wt% | 4.2 @1 kHz | 0.1 | 0.76[c)] | 93 | [131] |
| v-PDMS, addition cure | Pristine MMT | Mech. mix., US in heptane | 2 wt% | 5.8 @1 Hz | 0.001 | 0.166 | n.a. | [111] |
| v-PDMS, addition cure | Mod.[a)] MMT | Three roll mill | 30 phr | 10 @0.1 MHz | 0.008 | n.a. | 106 | [234] |
| Silastic 3481[b)] | MMT cloisite 15A | Low shear solvent mixing | 5 wt% | 4.2 @1 kHz | 0.1 | 0.76 | 93 | [132] |

[a)] γ-glycidoxypropyltimethoxysilane, γ-methacryloxypropyltimethoxysilane, stearic acid isopropyl trioleic titanate; [b)] Actuation stress 5.8 kPa @ 23 kV/mm for films of 450 µm thickness. Reduced relaxation time was observed for composites compared to pristine PDMS; [c)] At 25 % elongation.

*Table 5.* Conductive fillers.

| **Base elastomer** | **Filler** | **Method of dispersion** | **Content** | **ε'** | **tan δ** | **Y [MPa]** | **Max. strain [%]** | **Thickness of film for $E_B$ [μm]** | **$E_B$ [V/μm]** | **Maximum actuation strain [%]** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| v-PDMS | $BaTiO_3$ (100nm) and carbon black (50 nm)[a)] | THF, mech. mix. | 3 wt% C. black, 40 vol% $BaTiO_3$ | 40 @1 kHz | n.a. | 100 | n.a. | n.a. | n.a. | n.a. | [235] |
| Silastic 3481 | Expanded graphite | THF, US, SDBS | 1.6 wt% | 18.3 @1 kHz | 0.008 | 1.2 | n.a. | n.a. | n.a. | 2.5 @15 V/μm | [236] |
| v-PDMS, addition cure | MWCNT (d=10-20 nm, length 20 μm)[b)] | Xylene, US | 0.05 wt% | 3.56 @100 kHz | 0.00014 | 0.22-0.4 | 250 | n.a. | n.a. | 0.5 @28 V/μm | [141] |
| v-PDMS, UV cure by thiol-ene | MWCNT (d=10 nm, length 1.5 μm) | Speedmix.[c)] | 1 wt% | 4.5 @1 kHz | 0.006 | 0.05 | n.a. | 105-150 | 20 | n.a. | [149] |
| v-PDMS, addition cure | Expanded graphite | Speedmix. | 2 wt% | 4.5 @1 kHz | 0.09 | 0.002 | n.a. | 120-150 | 50 | 3.8 @42.5 V/μm | [237] |
| Rhodorsil MF620U | Functionalized graphene | Two-roll mixer | 1 wt% | 4.5 @10 Hz | 0.03 | n.a. | 644 | n.a. | n.a. | n.a. | [238] |

[a)] Carbon black and $BaTiO_3$ was modified with silane coupling agent KH550; [b)] Covalently functionalized with PDMS; [c)] Entrapped in a PDMS bimodal network

*Table 6.* Core-shell fillers used for DET applications.

| **Base elastomer** | **Filler** | **Method of dispersion** | **Content** | ***ε'*** | **tan δ @0.1 Hz** | **Y** | **Max. strain** | **Thickness of film for $E_B$** | **$E_B$** | **Maximum actuation strain** | **Ref** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **[MPa]** | **[%]** | **[µm]** | **[V/µm]** | **[%]** | |
| OH-PDMS, condens. cure | PANI in PDVB shell | Three roll mill, toluene | 15 vol% | 3.3 @100 Hz | 0.036[c)] | 0.39[d)] | 755 | n.a. | 50.9 | 12 @50 V/µm | [160] |
| OH-PDMS, condens. cure | PANI in PDVB shell | Three roll mill, toluene | 20 wt% | 3.4 @100 Hz | 0.05[c)] | 2.32 | >1000 | 100 | 43.4 | 15.5 % @43 V/µm | [161] |
| XLR630 | $TiO_2/SiO_2$ Aeroxide (STX801) | Speedmix. | 6 wt% | 3.88 @1 MHz | 0.005 | 0.187 | n.a. | 30-90 | 173 | n.a. | [147] |
| v-PDMS, peroxide cure | $SiO_2$/PDA/Ag/PDA[a)] | Two roll mill | 52 vol% | 48 @1 kHz | 0.004 | n.a. | n.a. | n.a. | n.a. | n.a. | [162] |
| PDMS, condens. cure | Ag/$SiO_2$ core shell particles 68 nm HMDS treated | Sonication, mechanical mixing | 20 vol% | 5.9 @1 kHz | 0.0078 | 1.44[b)] | 805 | 58 | 13.4 | 805 | [163, 164] |

[a)] PDA: Polydopamine. By use of the PDA layer it is possible to prevent percolation by control of shell thickness. Data given for 15 nm shell; [b)] Reported at 10% strain; [c)] @100 Hz; [d)] @10% strain.

*Table 7*. Properties of materials prepared as blends.

| **Base elastomer** | **Additive** | **Content** | ***ε'* @0.1 Hz** | ***ε'*@1 MHz** | **tan δ @0.1 Hz** | ***Y*** | **Maximum strain** | **Thickness of film for $E_B$** | **$E_B$** | **Maximum actuation strain** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | [MPa] | [%] | [μm] | [V/μm] | [%] | |
| TC-5005 A/B-C | Poly(3-hexylthiophene) | 1 wt% | 5.5[a)] | 3.8 | 0.14[a)] | 0.03 | 300 | 1000 | 8.5 | 7.6 @8 V/ μm | [167] |
| TC-5005 A/B-C (moisture cure) | PU | 40 vol% | 15.5[a)] | 5.2 | 0.6[d)] | n.a. | n.a. | 1000 | 5.5 | 2.7 % @5.5 V/ μm | [169] |
| SILASTIC 3481 | PEG (600 g $mol^{-1}$) | 5 phr | 5.4[b)] | 4.75[c)] | 0.03[b)] | 0.47[f)] | n.a. | 350 | 40 | 11.5 @40 V/ μm | [170] |
| MJK 4/13 | PEG-PDMS block copolymer | 5 wt% | 4.7 | 4.4 | 0.12 | 0.123[g)] | n.a. | <100 | 103 | n.a. | [171] |
| PDMS (DMS-V41) | Cyanopropyl-functional copolymer | 38.9 wt% | 17 | 6 | 0.25 | 0.25[e)] | n.a. | n.a. | 25 | 0.75 @8 V/ μm | [172] |
| Trifluoropropyl-divinylpolydimethylsiloxane | Fluorinated silicone oil | 45 wt% | 5.9 | 5.4 | 0.9 | 0.07[e)] | 270 | 250 | 22 | 4.2 @10 V/μm | [173] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LR3043/50 | Chloropropyl-functional silicone oil (LMS-152) | 30 phr | 4.4 | 4.4 | 0.004 | 1.35[f)] | 780 | 80 | 129.9 | n.a. | [174] |

[a)] @10 Hz; [b)] @100 Hz; [c)] @0.4 MHz; [d)] @1000 Hz; [e)] @10% strain; [f)] @5% strain; [g)] Calculated from storage modulus, *G'*, where $Y = 3G'$.

*Table 8.* Properties of chemically modified silicone dielectric elastomers.

| **Base elastomer** | **Additive** | **Content** | ***ε'*@0.1 Hz** | ***ε'*@1 MHz** | **tan δ @0.1 Hz** | ***Y*** **[MPa]** | **Maximum strain [%]** | **Thickness of film for $E_B$ [µm]** | **$E_B$ [V/µm]** | **Maximum actuation strain [%]** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PDMS (DMS-V31) + HMS-301 cross-linker | *N*-allyl-*N*-methyl-*p*-nitroaniline | 13.4 wt% | 19 | 5.9 | 2 | 0.41[b)] | n.a. | 80 | 39 | 1.25 @15.5 V/µm | [176] |
| PDMS (DMS-V41) + HMS-301 cross-linker | *N*-allyl-*N*-methyl-*p*-nitroaniline | 13.4 wt% | 14 | 5 | 1 | 0.25[c)] | 680 | n.a. | 25 | 0.5 @7 V/µm | [177] |
| Sylgard 184 | *N*-allyl-*N*-methyl-*p*-nitroaniline | 10.7 wt% | 10.1 | 6.2 | 0.4 | 0.85[c] | 350 | n.a. | 61 | 3 @28 V/µm | [178] |
| Elastosil RT625 | *N*-allyl-*N*-methyl-*p*-nitroaniline | 10.7 wt% | 8 | 5.6 | 1 | 0.142[c)] | 170 | n.a. | 31 | 2 @10 V/µm | [178] |
| OH-PDMS | OH-Cyanopropyl-functional siloxane copolymer | 28 wt% | n.a. | 3.5 | n.a. | 0.71[c)] | 228 | 150 | 42 | 10 @40 V/µm | [179] |
| OH-PDMS | OH-Cyanopropyl-functional | 27 wt% | 12[d)] | 4.5 | 5[a] | 0.8[c)] | 170 | n.a. | 56 | 8 @56 V/µm | [181] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | siloxane copolymer | | | | | | | | | | |
| PDMS (DMS-H21) | Nitrobenzene and azonitrobenzene on synthesized cross-linker | 0.5 wt% | 3.3 | 3.3 | 0.0006 | 0.167[e)] | n.a. | 150 | 92 | n.a. | [182] |
| Synthesised azido-functional siloxane copolymers | Nitrobenzene | 5.6 wt% | 14.2 | 5.0 | 6.5 | 0.08[f)] | n.a. | 75 | 69.2 | n.a. | [239] |
| OH-PDMS | R-trialkoxysilanes as functional cross-linkers | 15 wt% | 3.2[a)] | 3.15 | 3.45[a)] | 0.723[c)] | 180 | 600 | 0.63 | 3 @0.63 V/µm | [187] |
| OH-polymethylvinylsiloxane | 3-mercaptopropionitrile | 48 wt% | 10.1 | 40 | 10 | 0.15[c)] | 260 | ~1200 | 10.8 | 20.5 @10.8 V/ µm | [188] |
| OH-PDMS | Dihydroxyl-nitroazobenzene | 7.1 wt% | n.a. | 4.64 | n.a. | 0.325[f)] | 375 | 170 | 70.0 | 17 @68 V/µm | [190] |
| Synthesized copolysiloxanes | Chloropropyl-groups | 10 wt% | 4.9 | 4.7 | 0.02 | 1[g)] | 125 | 80 | 94.4 | n.a. | [191] |

[a)] @1 Hz; [b)] @ small strains and calculated from the elastic modulus, $M_{Act}$, where $Y = M_{act}*4/3$; [c)] @10% strain; [d)] @10 Hz
[e)] Calculated from stated storage modulus, $G'$, where $Y = 3G'$; [f)] @ small strains; [g)] @5% strain.

*Table 9.* Properties of interpenetrating and bimodal networks.

| **Type** | **Base elastomer** | **Additive** | **Content** | **$\varepsilon'$ @0.1 Hz** | **$\varepsilon'$@1 MHz** | **tan δ @0.1 Hz** | ***Y*** | **Maximum strain** | **Thickness of film for $E_B$]** | **$E_B$** | **Maximum actuation strain** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **[MPa]** | **[%]** | **[µm]** | **[V/µm]** | **[%]** | |
| IPN | VHB-4910 film | Sylgard-184 (addition cure) | 50 wt% | n.a. | n.a. | n.a. | 0.25 | 850 | n.a. | n.a. | 120 @72 V/µm[d)] | [197] |
| IPN | VHB-4910 film | Elastosil E-43 (moisture cure) | 50 wt% | n.a. | n.a. | n.a. | 0.25 | n.a. | n.a. | n.a. | 100 @72 V/µm[d)] | [197] |
| IPN | Dow Corning HSIII (moisture cure) | Elastosil LR 3003/70 (addition cure) | 15 wt% | n.a. | n.a. | n.a. | 0.54 | 500 | n.a. | 55 | 25 @55 V/µm | [63] |
| IPN/bimodal | OH-PDMS | Vinyl-PDMS | 50 wt% | 3.2[a)] | 3.0 | 5.8[a)] | 0.35[c] | 433 | 210 | 48 | 7.9 @40 V/µm | [198] |
| IPN | Elastosil LR3043/30 | Amino-functional PDMS (AMS-162)+ carboxydecyl-terminated PDMS (DMS-B12) | 90 wt% | 2100 | 4.1 | 2.3 | 0.035[b)] | n.a. | 40-100 | 87 | n.a. | [201] |
| Bimodal | DMS-V35 | DMS-V05 | 10 wt% | n.a. | n.a. | n.a. | 0.06[b)] | n.a. | n.a. | n.a. | n.a. | [215] |
| Bimodal | DMS-V35, DMS-V05 and (mercaptopropyl) methylsiloxane-dimethylsiloxane copolymer (GP | Multi-walled carbon nanotubes (MWCNT) | 1 wt% | 4.7 | 4.5 | 0.025 | 0.165[b)] | n.a. | 105–150 | 20 | n.a. | [149] |

367) as cross-
linker

[a)] @1 Hz; [b)] Calculated from stated storage modulus, *G'*, where $Y = 3G'$; [c)] @10% strain; [d)] Determined from stress-strain curves coupled with actuation data.

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**Silicone elastomers are favourable materials for dielectric elastomer transducers (DETs),** but for the field to progress, a leap in material development is required and it is essential that all aspects of the elastomer are taken into account. In this review the current state of silicone elastomers for DETs is summarised and critically discussed.

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**The current state of silicone-based dielectric elastomer transducers**